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VINYL CHLORIDE

AN ASSESSMENT OF EMISSIONS CONTROL TECHNIQUES AND COSTS

RESEARCH TRIANGLE INSTITUTE

PREPARED FOR

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16. ABSTRACT

The report gives results of a survey of conceptual techniques applicable to vinyl chloride monomer (VCM) emission reduction with respect to VC monomer and polymer production. VCM emission points have been identified and quantified for four types of monomer plants--hydrochlorination of acetylene, chlorination/oxychlorination of ethylene (with oxygen) and dehydrochlorination, and direct chlorination of ethylene and dehydrochlorination--and four types of polymer manufacture--suspension polymerization, emulsion polymerization, bulk polymerization, and solution polymerization. Levels of control achievable and estimated cost of listed control techniques are presented.

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This document is a compilation and assessment of the vinyl chloride emission sources and controls in the monomer and polymer segments of the industry. The assessment was carried out under the direction of Dr. Dale A. Denny, and the technical direction of Mr. Kenneth Baker. It is based upon data presented by manufacturers in June 1974.

Major contributions were made by a team of scientists: Ben H. Carpenter (Research Triangle Institute), Stanley E. Dale (A. D. Little, Inc.), J. J. Kearney (RTI), Richard A. Markle (Battelle), and C. J. Santhanam (A. D. Little, Inc.). At RTI, Kay Marr provided editing. Ronnie Davis and Walter Williams, III, provided drafting and Anne Inscoe typed the manuscript.

VINYL CHLORIDE

An Assessment of Emissions Control Techniques and Costs

1. INTRODUCTION

1.1 PURPOSE AND SCOPE

The purpose of this study is to provide an assessment report on vinyl chloride emissions from monomer and polymer processes currently existing in the United States. The assessment is based on information supplied at this time (June 18, 1974) by manufacturers in response to Mr. Don R. Goodwin's letter of request, written under the authority of the Federal Clean Air Act (42 U.S.C. section 1857 et seq.). Requested process flowsheets were not yet available. Requested cost data generally were not clearly defined. For these reasons, simplified flowsheets were prepared to describe the sources of emissions for the different processes; these led to a listing of sources, which served as a framework for first tabulating and then assessing control methods. The study results are tentative. They could be altered or contradicted by data that accrue as manufacturers continue to respond. For the extent of data, however, the assessments are believed to be valid.

1.1.1 Process Types

Vinyl chloride monomer (VCM) processes are of four types: (1) hydrochlorination of acetylene; (2) chlorination-oxychlorination of ethylene (using air) and dehydrochlorination; (3) chlorination-oxychlorination of ethylene (using oxygen) and dehydrochlorination; and (4) direct chlorination

of ethylene. Two VCM production processes--hydrochlorination and dehydrochlorination are represented by the acetylene-hydrogen chloride reaction

$$HC{\equiv}CH + HCl \longrightarrow H_2C{=}CHCl$$

and the thermal dehydrochlorination of 1,2-dichloroethane

$$ClCH_2{-}CH_2Cl \longrightarrow H_2C{=}CHCl.$$

Two VCM plants use the hydrochlorination of acetylene process. The plants using dehydrochlorination of ethylene dichloride (EDC) usually are integrated with an EDC production unit, but the plant processes for producing EDC differ. Nine plants use the balanced oxychlorination process: ethylene is chlorinated by a mixture of pure chlorine and chlorine produced by the oxidation of hydrogen chloride, which is recycled from the cracking of EDC. One plant uses a modified balanced oxychlorination process: oxygen instead of air is used to oxidize the hydrogen chloride to chlorine. Three plants use the direct chlorination process: ethylene is chlorinated and dehydrochlorinated, but the hydrogen chloride from the dehydrochlorination step is not recycled. The 15 plants have a production capacity of 6.8 billion pounds of VCM.

Polyvinylchloride (PVC) production capacity at 37 plant sites totals (by name) 4.75 billion pounds a year. There are four production processes--(1) suspension polymerization (78% of total production); (2) emulsion polymerization (12%); (3) bulk polymerization (6%); and (4) solution polymerization (4%).

1.1.2 Process Emissions

Emissions of gaseous VCM occur at both VCM and PVC resin plants. This VCM is distributed into the atmosphere surrounding the plant sources. The

emissions patterns depend on the amount of VCM released, the nature of the plant area from which it is released, and the meteorological conditions. The concentrations occurring in residential areas are not known at the present time, but appear to be mostly below 1 part per million (ppm). If control at lower air concentrations becomes necessary, this will have to be accomplished by limiting the VCM emissions at the plant sources. The level of VCM which may be considered safe has not been determined. Until April of 1974, the acceptable level was approximately 500 ppm; since April, an emergency standard of 50 ppm has been established.

Since the accumulated data for this study show that 1973 production capacities were 6.8 billion pounds of VCM and 4.75 billion pounds of PVC resin and that PVC manufacturers are operating at full capacity in 1974, it must be assumed that present production is either equal to or greater than the 1973 capacities. Analysis of the data so far supplied to EPA by VCM and PVC producers show that total VCM emissions escaping to the atmosphere is on the order of 156-210 million pounds per year. Of the total VCM, over 90 percent is from PVC production facilities, as shown in Table 1-1.

VCM-producing companies are listed in Table 2-1. Included are their geographical locations, population figures for adjacent communities, and

Table 1-1. VCM AND PVC PRODUCTION AND VCM EMISSIONS ESTIMATES, 1973

Plant Type	Production Capacity (MM lbs/yr)	VCM Emitted (MM lbs/yr)	VCM Emitted (% of production)
VCM	6,800	14-20.4	0.2-0.3
PVC	4,750	142-190	3-4
Total		156-210	

calculated VCM emissions levels. PVC producers are similarly listed in Table 3-1.

The VCM emissions from PVC plants are at least 10 times as copious as those from VCM plants. This comparison is based on data supplied by relatively few (7) companies. The reporting companies state that the emission figures were arrived at by measurements, estimates, and guesses. In no case has it been possible to calculate overall material balances. Thus the accuracy of the VCM emissions data cannot as yet be assessed.

The lower VCM emissions levels (pound per pound of product) at VCM plants are partially offset by the fact that these plants usually have appreciably larger production capacities than PVC plants. The net result is that the absolute VCM emissions levels from PVC plants are usually 2 to 5 times higher than those of VCM plants.

All data received have shown a large fraction of total VCM emission losses as fugitive losses (30-50 percent) with no breakdown of individual emission points. Fugitive losses should be presented as an aggregate of small losses from valves, packing glands, pump seals, agitator seals, compressor seals, flange connections, safety valves, piping leaks, and instrument connections. Total fugitive losses should be not more than about 10 percent of total.

Two other features of the industry are significant in terms of potential VCM concentration levels in the atmosphere near plants: (1) VCM plants are to some extent clustered in areas along the Texas-Louisiana Gulf Coast and (2) PVC plants tend to be located either close to/or adjacent to VCM production sites. Clustering of plants is greatest near Pasadena-Deer Park, Texas, and Baton Rouge, Louisiana. In Table 1-2,

Table 1-2. COMPARISON OF VCM EMISSIONS BY CLUSTERS OF VCM AND PVC PRODUCERS

Company Name and Location		City Population (1970 census)	Name Plate Production Capacity (MM lb/yr)	VCM Emissions[a] (MM lb/yr)	Type of Process[b]
Allied Chemical	Baton Rouge, La	165,963[c]	300	0.9	B
Dow Chemical	Plaquemine, La	7,739[d]	340	1.0	DC
Ethyl Corporation	Baton Rouge, La	165,963[c]	270	0.8	B
Ethyl Corporation (Indus Chem Div)	Baton Rouge, La	165,963[c]	180	7.2	S
Georgia Pacific	Plaquemine, La	7,739[d]	200	8.0	U
The Goodyear Tire & Rubber Co (Chem Div)	Plaquemine, La	7,739[d]	100	4.0	S
Monochem, Inc	Geismar, La	7,739[d]	300	0.9	A
Total			1690	22.8	
Continental Oil	Lake Charles, La	77,998	600	1.8	B
P.P.G. Industries	Lake Charles, La	77,998	300	0.9	B
Shell Chemical	Narco, La		700	2.1	B
Certainteed Corp	Lake Charles, La	77,998	200	8.0	U
Total			1800	12.8	
Diamond Shamrock Corp (Chem Co Plas Div)	Deer Park, Tex	12,773[e]	250	10.0	S&E
Ethyl Corporation	Pasadena, Tex	89,277[e]	150	0.5	DC
Shell Chemical	Deer Park, Tex	12,773[e]	875	2.6	B
Tenneco Chemical	Pasadena, Tex	89,277[e]	250	0.8	A
Union Carbide Corp (Chem & Plas Div)	Texas City, Tex	38,908	200	8.0	S
Total			1725	21.9	
Dow Chemical	Freeport, Tex	11,997[f]	180	0.5	DC
Dow Chemical	Oyster Creek, Tex	11,997[f]	800	2.4	B
Shintech	Oyster Creek, Tex	11,997[f]	250	10.0	U
Total			1230	12.9	

[a] Extrapolations based on estimated 0.3% VCM atmospheric emission loss from VCM produced, and on 4% from PVC produced.

[b] A, chlorination of acetylene; B, chlorination-oxychlorination, with HCL from cracking recycled to oxychlorination; DC, direct chlorination; E, emulsion polymerization; S, suspension polymerization; U, unknown (under construction).

[c] Baton Rouge Parrish (county) - 302,031.

[d] Plaquemine Parrish (county) - 25,225.

[e] Harris County - 1,741,912.

[f] Brazoria County - 108,312.

geographically clustered VCM and PVC producers are listed together for comparison.

1.1.3 Emissions Controls

Emissions control equipment used in the state of the art is often a basic part of the processing system, thus it serves primarily to recover a reactant or a product. State of the art controls are appraised herein by using performance data from the VCM and the PVC manufacturers or by comparing the emissions levels of one plant with and one plant without controls. Controls so appraised include recycling, condensation with refrigeration, compression, adsorption, incineration, oxidation with ozone, scrubbing (absorption), and venting to flares.

1.1.3.1 Recycling

Recycling is used in the balanced EDC process to return EDC vapors vented from oxychlorination units to the recovery units of the direct chlorination systems and to recycle the vent stream from the VCM light-ends column to the oxychlorination reactor. Recycling eliminates the need for additional recovery systems and reduces the total number of emissions sources, but it carries VCM back to early process stages where VCM emissions would not be expected to occur otherwise.

1.1.3.2 Condensation

Since many process vent streams contain hydrocarbons, acids, and low-molecular-weight chlorinated hydrocarbons as well as VMC, the condensation via heat exchange is used for recovery of material and, often incidentally, for emissions control. When vent streams contain water vapor, condensation is carried out at the lowest practical temperature consistent with keeping the water from freezing on the condensor. When vent streams do not contain

water vapor, refrigeration can be used for more effective control. The low boiling point of VCM, however, imposes a natural limit to the ultimate effectiveness of condensation. Temperature and pressure limits must be maintained to prevent hazardous reactions (explosions) in the recovery system because VCM is a reactive gas. Due to its flammability, the gas must be handled in nonoxygen-containing streams, and most of the recovery efforts must be made without exposure to air. When vent gases from the acetylene-hydrogen chloride reactor are cooled to below 40°F at 35 psig to recover VCM and then scrubbed (water) to remove hydrogen chloride (HCl), about 85 percent of the VCM is removed by condensation.

1.1.3.3 Compression

Compression is used in controlling emissions in transfer operations, in reducing the costs of refrigerated condensation units, and in combination with condensation to help control emissions from reactor units. Overhead vapors from receiving tanks are compressed, condensed, and recycled to the tank car (or barge) being unloaded. Vent gases from PVC reactors may contain 80 percent VCM after passing a water-cooled condenser (85°F). A refrigerated condenser (40°F) would reduce the VCM emissions by 35-40 percent; at lower temperatures, water vapor, if present in sufficient concentration, tends to freeze on the condenser surfaces. Condensation at 40°F with compression to 40 psig would reduce the VCM emissions by an estimated 60-75 percent, and further compression to 80 psig would reduce them an estimated 80-90 percent.

1.1.3.4 Adsorption

In general, adsorption is recognized as the most efficient control method for achieving low concentrations of organic emissions in air. Use

of such a "concentrating device" could drastically reduce energy costs involved in the compression and refrigeration cycles normally required to condense dilute streams of fugitive VCM efficiently. Adsorption on activated carbon (or another sorbent) should effect an estimated 90 percent or better reduction in the VCM content of vented process gases. Use of adsorption requires a system with provisions for regeneration of the sorbent bed (desorption) and provision for recovery or disposal of the VCM. Two or more adsorbers may be installed in parallel for alternate use and regeneration. Desorption of VCM with hot inert gases permits recovery or incineration of the vapors. Desorption may be accomplished with steam, followed by condensation and phase separation.

Adsorption is indicated for use as a final control for vent gases already subjected to condensation and/or scrubbing. Little experience has been reported in these uses, however, and concern has been expressed that polymerization of VCM on the carbon surface might reduce its capacity substantially.

1.1.3.5 Incineration

Incineration is used to oxidize hydrocarbon contaminants to carbon dioxide and water. During combustion, chlorinated hydrocarbons with hydrogen-to-chlorine ratios of at least 5:1 yield hydrogen chloride; those with ratios less than this yield chlorinated hydrocarbons which are difficult to collect. Downstream from the incinerator, either absorption equipment (e.g., caustic gas scrubbers) or possibly a recovery process is required to extract the hydrogen chloride produced during combustion of VCM, PVC, or other chlorinated compounds. Both incinerators and afterburners can oxidize influent VCM at nearly 100 percent efficiency. Cycling afterburners can be used

with adsorbers to conserve fuel; during desorption, the afterburner incinerates the stripped VCM. A regenerative heat exchanger can be used to preheat the influent, conserve fuel, and defray costs.

1.1.3.6 Oxidation with Ozone

Ozone oxidation is considered appropriate only for streams with a few ppm's concentration because this process is expensive. As a clean-up method, it is appropriately used after application of other techniques to achieve complete elimination of VCM.

1.1.3.7 Scrubbing

Scrubbing with high-impact water streams is generally used to remove hydrogen chloride and some EDC from vent streams. Absorbents other than water (lean oil, red oil, kerosene, and chlorinated hydrocarbons) might be practical for removing VCM from oxygen-free streams, but the scrubbing system would be large and would have to be operated at several atmospheres of pressure to permit practical solvent rates, so operating costs would be high.

1.1.3.8 Venting to Flares

VCM vented to and burned in flares releases hydrogen chloride, which is also a pollutant. Flares are, therefore, a questionable control technique and should be considered primarily for emergency control. Since flaring usually requires supplemental fuel, the cost varies with fuel prices.

1.1.3.9 Longer term Controls

Longer term controls are those the use of which requires development effort and comparative evaluation. Included are process modifications and washing with EDC. Some oxychlorination systems may profit from the addition of a postchlorination unit which would presumably eliminate VCM

by chlorinating it along with any unreached ethylene. In practice, vent streams other than the oxychlorinator effluent would be fed to this unit. From direct chlorination systems, eligible feeds include: the direct chlorination reactor vent, the water-wash vents, and the light-ends column vent. Crude EDC may be an effective absorbent for VCM in vent gases; the possibility requires investigation.

1.1.4 Control Costs

Control costs presented herein were supplied by manufacturers. Generally, only capital investment costs are given. In some cases, annual operating and maintenance costs are included. No standardization of cost elements was achieved because data were too sparse; the data received appeared to have been based on estimates for the particular process using cost elements (e.g., labor) appropriate for the location. When ranges of cost are shown, they should be regarded as best approximations only.

1.2 REPORT ORGANIZATION

The assessment is divided into two main parts--VCM processes and PVC processes. Each of eight major processes is discussed as a separate entity. Emission points are identified using simplified flow diagrams. Their controls are discussed in terms of the emission source characteristics, and cost estimates are given where available. The findings are summarized, and research and development needs are indicated.

2. VINYL CHLORIDE MONOMER

2.1 OVERVIEW OF VCM PROCESSES

Table 2-1 lists VCM producers to show published production capacities and VCM estimated emissions by process type and location.

Table 2-1. VCM PLANT EMISSION DATA

Company Name and Location	City Population (1970 census)	Name Plate Production Capacity (MM lb/yr)	VCM Emissions[a] (MM lb/yr)	Type of Process[b]
Allied Chemical, Baton Rouge, La	165,963[c]	300	0.9	B
American Chemical, Long Beach, Calif	358,633[d]	170	0.5	B
Continental Oil, Lake Charles, La	77,998	600	1.8	B
Dow Chemical, Freeport, Tex	11,997[e]	180	0.5	DC
Dow Chemical, Plaquemine, La	7,739[f]	340	1.0	DC
Dow Chemical, Oyster Creek, Tex	[e]	800	2.4	B
Ethyl Corporation, Baton Rouge, La	165,963[c]	270	0.8	B
Ethyl Corporation, Pasadena, Tex	89,277[g]	150	0.5	DC
B. F. Goodrich, Calvert City, Ky	31,627[h]	1,000	3.0	B
Monochem Inc, Geismar, La	7,739	300	0.9	A
P.P.G. Industries, Lake Charles, La	77,998	300	0.9	B
P.P.G. Industries, Guayanilla, PR		575	1.7	U
Shell Chemical, Deer Park, Tex	12,773[g]	875	2.6	B
Shell Chemical, Narco, La		700	2.1	B
Tenneco Chemical, Pasadena, Tex	89,277[g]	250	0.8	A
Total		6,810	20.4	

[a] Extrapolations based on estimated 0.3% of VCM production lost to atmosphere.

[b] A, chlorination of acetylene; B, chlorination-oxychlorination, with HCL from cracking recycled to oxychlorination; DC, direct chlorination; U, unknown.

[c] Baton Rouge Parrish (county) - 302,031.

[d] Los Angeles County - 7,032,075.

[e] Brazoria County - 108,312.

[f] Plaquemine Parrish (county) - 25,225.

[g] Harris County - 1,741,912.

[h] Population of Paducah, Ky.

2.2 HYDROCHLORINATION OF ACETYLENE

Two plants are reportedly producing VCM by the hydrochlorination of acetylene. This process accounts for 8 percent of the total VCM production.

2.2.1 Emission Points

The VCM is produced by the hydrochlorination of acetylene (Figure 2-1) using a mercuric chloride catalyst. The product gases are compressed, cooled, and pumped to a purification system consisting of a light-ends distillation column and a heavy-ends distillation column. The light-ends are passed to a vent-gas reactor, from which the product is recycled to the purification system; the heavy-ends are transferred to a temporary storage tank and eventually incinerated.

The main sources of emissions are (1) the reactor condenser vent, (2) the scrubber vent, (3) the VCM product-loading facility, and (4) the heavy-ends storage vent. The vent-gas reactor vent and the scrubber are continuous emission sources, the others are intermittent. The instantaneous rate of loss in the loading system may be 1-2 times greater than that in the purification system, but the VCM loss per million pounds of VCM produced is greater in the purification system.

The emission sources listed in Table 2-2 correspond with operational steps in a generalized hydrochlorination process. The data on plant production and emission rates are calculated values; their reliability cannot be estimated from information presently available. Fugitive sources (pumps, pump maintenance, valves, pressure relief valves, samplers) were not identified separately by the manufacturers, so the value quoted is an estimated total. Estimates of emissions resulting from upset conditions

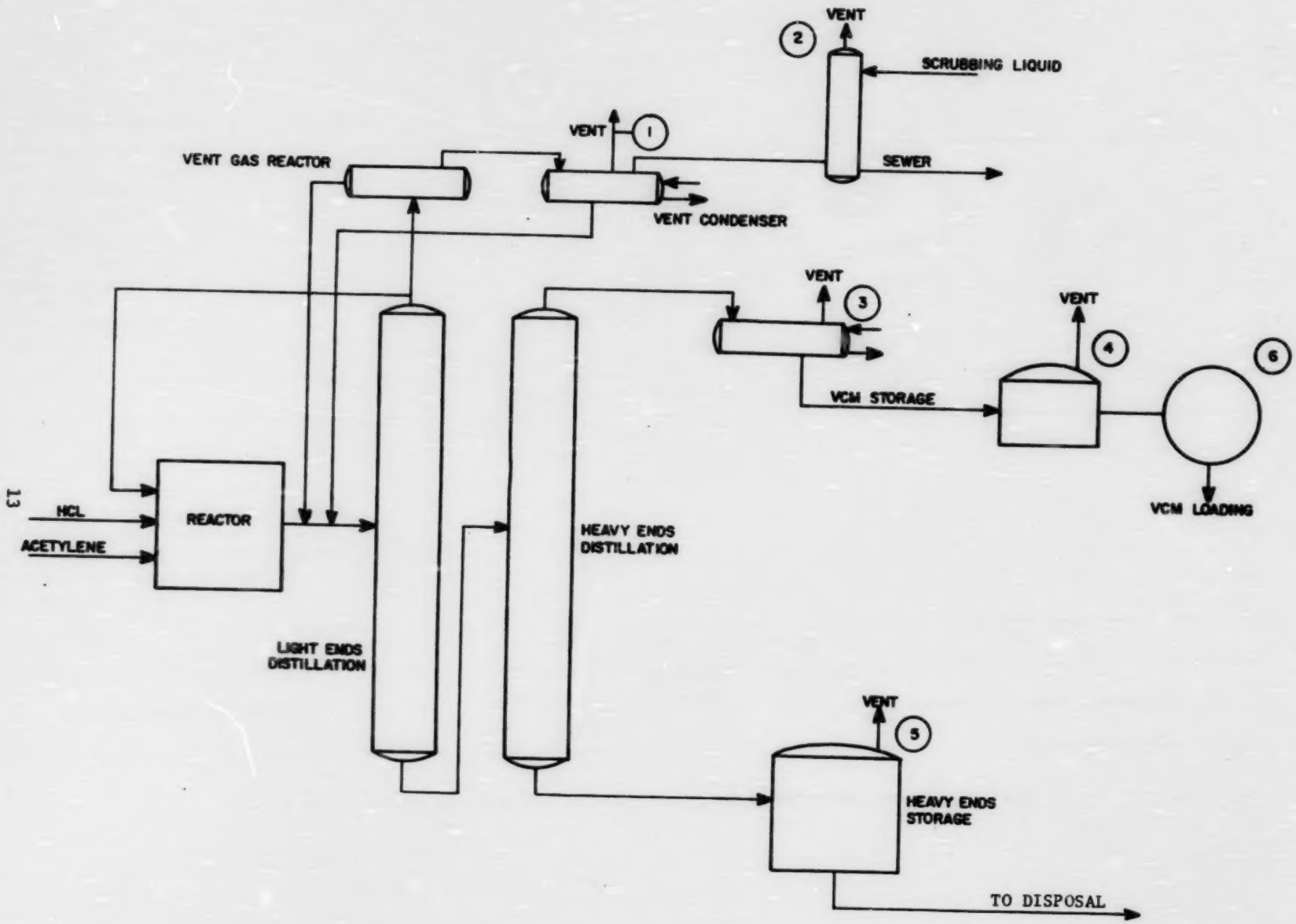

FIGURE 2-1 SIMPLIFIED FLOW SHEET ACETYLENE TO VINYL CHLORIDE PROCESS

Table 2-2. EMISSION RATES FOR VCM PROCESS 1: HYDROCHLORINATION OF ACETYLENE

PROCESS EMISSION SOURCE[a]	PLANT A			Comment on Plant Operation
	lb VCM/MM lb produced	lb VCM/hr emitted	%VCM emissions	
Production Sources Emitting VCM				
1. Vent-gas reactor vent, C	3528	117.5	61	
2. Vent-gas scrubber vent, C				
3. Heavy-ends distillation column vent, I				
4. VCM storage tank vent, I				
5. Heavy-ends storage tank vent, I	750		13	
6. VCM-loading facility, I				
Total	4278	117.5	74	
Fugitive Sources Emitting VCM				
Pumps, C				
Pump maintenance, I				
Valves, C				
Relief valves, C				
Flange connections				
Samplers, C				
Miscellaneous				
Total	1500	50.0	26	

[a] C is continuous, I is intermittent.

were generally not available, so no values appear in the table; furthermore, the quantities of these emissions depend on the efficiency of operation and quality of maintenance and thus would not be generally applicable from plant to plant.

2.2.2 Controls and Costs

The level of VCM can be reduced with state of the art controls to significantly below 50 ppm. Selection of a control method depends on the size of the emission source and the reduction level desired. Fugitive sources must be identified before making a choice of controls available to reduce individual emissions to any specified level.

The state of the art controls should be applicable to existing acetylene-hydrogen chloride plants. The phasing out of this acetylene-dehydrochlorination process and the likelihood that state of the art controls will suffice to bring this process under good control obviate the need for consideration of long-term controls.

The costs of reducing VCM emissions to <50 ppm have been provided by some producers and have been estimated for other emission sources for which data were provided. The estimates consist mainly of equipment and instrumentation costs. Installation and labor costs vary with plant makeup and location and therefore have not been included. In general, the costs for reducing a major VCM emission stream (100-500 lbs/hr) by 99 percent range from $50,000 to $100,000, as shown in Table 2-3.

2.3 CHLORINATION-OXYCHLORINATION OF ETHYLENE (WITH AIR) AND DEHYDRO-CHLORINATION

The balanced oxychlorination process (Figures 2-2, 2-3, 2-4) for the production of EDC is the principal one used in this country in the manufacture of

Table 2-3. CONTROLS AND COSTS FOR VCM PROCESS 1: HYDROCHLORINATION OF ACETYLENE

Emission Source Control	Percent Emission Reduction	Control Cost Estimate	Comment
1. Vent-Gas Reactor Vent: continuous stream; 40°F, 35 psi			
Refrigerated condenser, HCL scrubber	85	$50,000	Plant A.
Carbon bed adsorber	99	$50,000	Cost + installation + adsorbent.
2. Vent-Gas Scrubber Vent: continuous stream; 50-100°F			
3. Heavy-Ends Distillation Column Vent: intermittent stream			
4. VCM Storage Tank Vent: intermittent stream			
5. Heavy-Ends Storage Tank Vent: intermittent stream			
6. VCM-Loading Facility: intermittent stream			
Fugitive Sources: continuous stream			
Pumps			
Pressurized mechanical seals	95		
Valves and relief valves			
Diaphragm valves	95		
Double lock valves	50		
Samplers (collectors)	90	$1,000	
Miscellaneous			
Preventive maintenance	50	$40,000	Cost of 1/2 man-year labor.

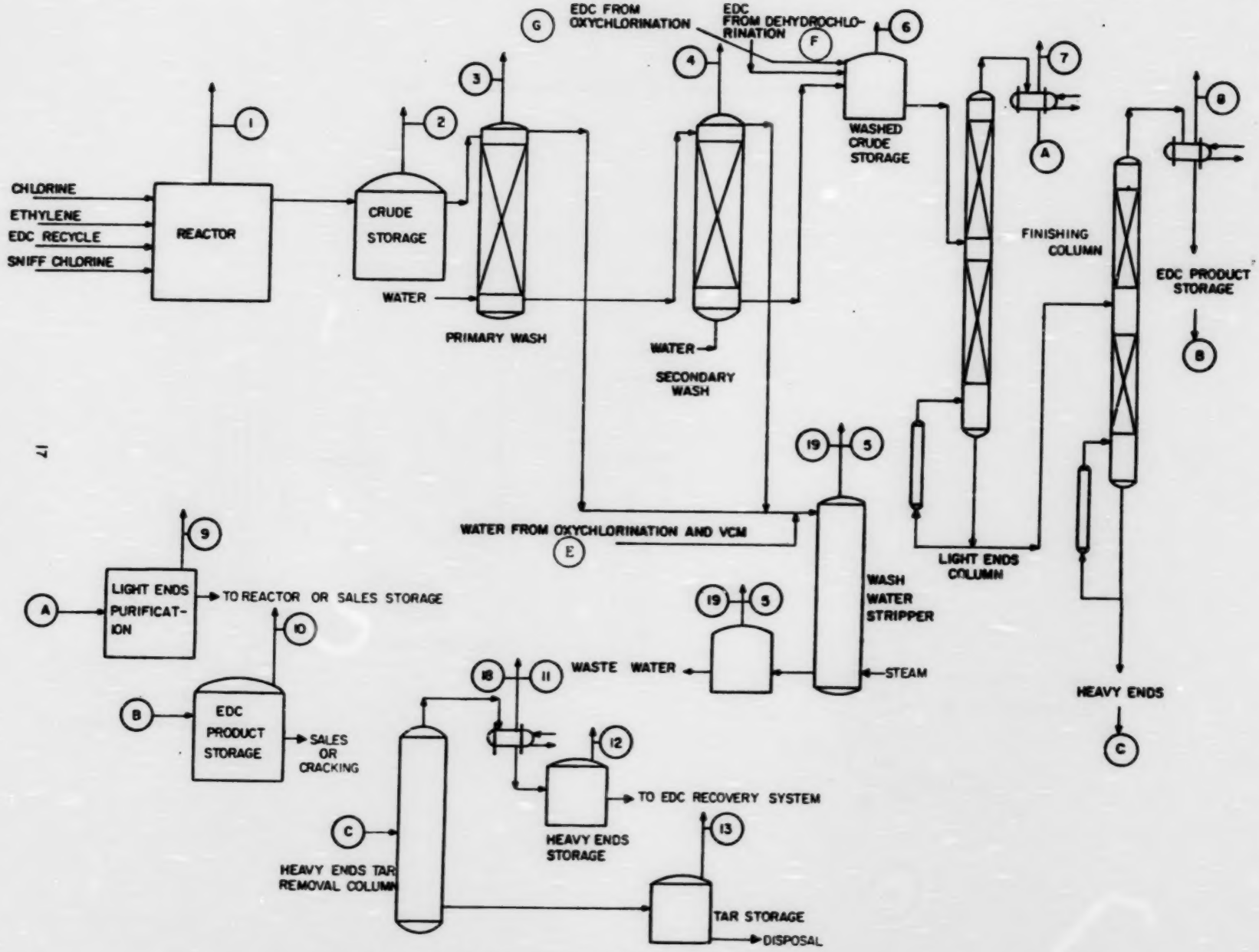

FIGURE 2-2 ETHYLENE DICHLORIDE FROM ETHYLENE AND CHLORINE

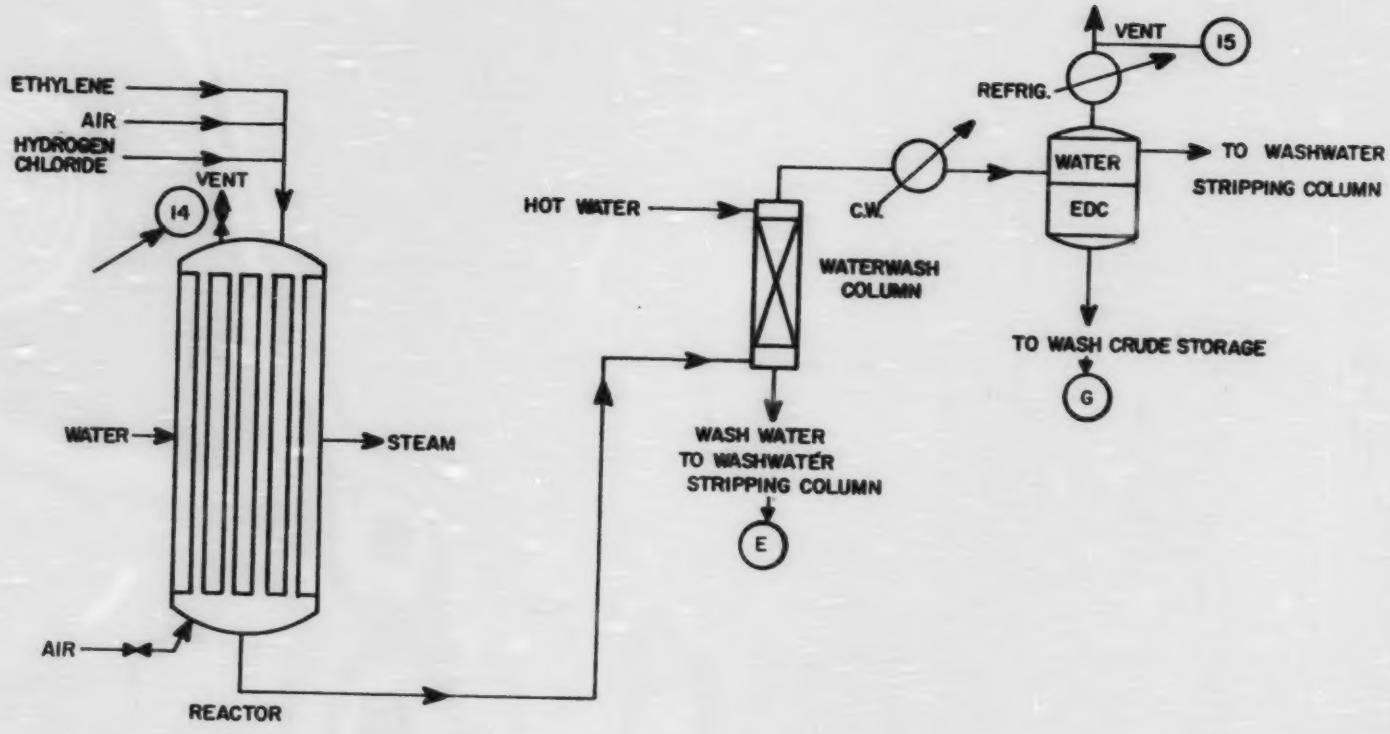

FIGURE 2-3 ETHYLENE DICHLORIDE FROM ETHYLENE + HCL + AIR

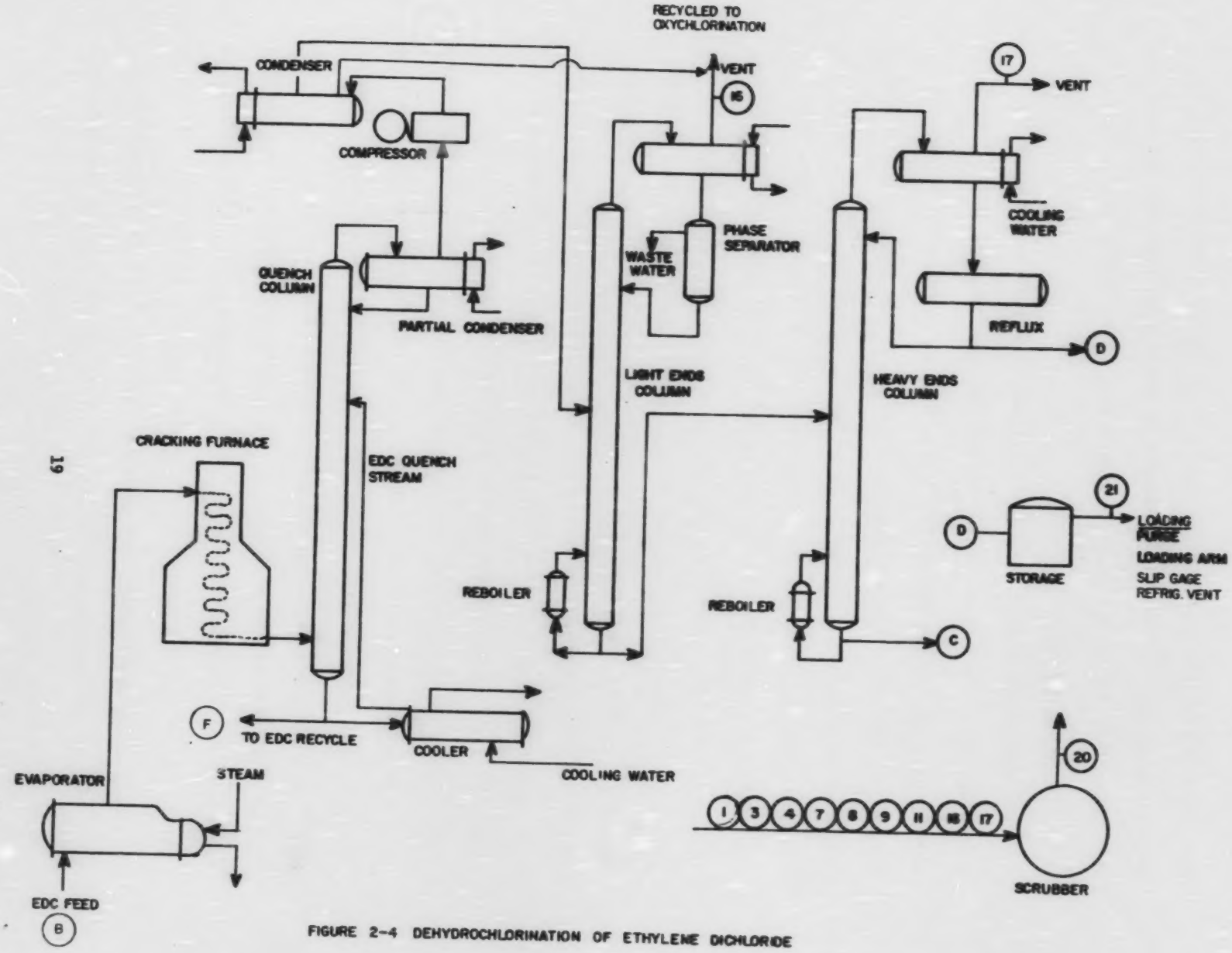

FIGURE 2-4 DEHYDROCHLORINATION OF ETHYLENE DICHLORIDE

VCM. Currently, nine plants using this process produce 5015 million pounds a year, accounting for 74 percent of total VCM usage and approximately 77.5 percent of the 20.4 million pounds a year of VCM emissions.

2.3.1 Emission Points

The VCM manufacturing operations discussed in this section use two processes--direct chlorination for making EDC from ethylene and chlorine, and oxychlorination for making EDC from ethylene, hydrogen chloride, and oxygen from the air. The EDC intermediate product is cracked to VCM during dehydrochlorination.

During direct chlorination, the inerts in the chlorine feed are vented from the crude EDC (after refrigeration of the gas) and the catalyst is washed away with water. During the oxychlorination, about 98 percent of the ethylene is converted to EDC, and the gases from the reactor are cooled to condense the product, then washed with water (or an aromatic solvent) to remove hydrogen chloride, and vented to the atmosphere.

Crude EDC produced by the two processes is combined with recycled crude EDC from cracking recovery and subjected to final distillation to remove light and heavy ends. Refined EDC may be sold. If processed to VCM, pure EDC is transferred to the VCM section of the plant, where it undergoes thermal dehydrochlorination (cracking) as it passes through empty or packed tubes (tubes packed with charcoal, pumice, or similar materials) at 900-950°F and at pressures of 50-300 psig. The reactor gases (VCM, EDC, and hydrogen chloride) are quenched in a column and transferred to a light-end distillation column, where the hydrogen chloride is stripped off and recycled to the oxychlorinator. (In some plants, the hydrogen chloride is removed by scrubbing with water; the noncondensibles are removed from the column top; and EDC,

from the bottom.) Then, the product stream undergoes a number of distillation steps to remove both heavy and light ends (a drying column is sometimes included in this sequence). The final product, normally VCM, is transferred to storage and finally to loading facilities.

The VCM emissions occur not only during the dehydrochlorination but also, to a lesser extent, during the manufacture of EDC; in the last case, emissions occur because of side reactions and because of VCM recycling. The main dehydrochlorination sources of VCM are the purification system vents, the scrubber tower vent, and the loading facility vents. Losses from the purification system are continuous; those from the loading system are intermittent. The instantaneous rate of VCM from loading loss may be 1-2 times greater than that from the purification process, but the VCM loss per pound of VCM produced is greater for purification. Emission sources listed in Table 2-4 are sequenced to correspond with successive steps in a generalized processing operation. Fugitive sources (pumps, pump maintenance, valves, waste water, pressure relief valves, samplers, etc.) are indicated separately, since their exact location throughout the system will vary from plant to plant. The sources shown were chosen to provide a checklist for tabulating and comparing data from several plants. The practices for handling vent and waste streams--namely, the recycling, the combining of vented gases into single streams, and the varying of numbers of reactors and storage tanks--presented special problems for tabulating available data.

The reliability of the data in the table depends on whether they have been measured or calculated. The VCM concentrations, commonly measured

Table 2-4. EMISSION RATES FOR VCM PROCESS 2: CHLORINATION-OXYCHLORINATION OF ETHYLENE (WITH AIR) AND DEHYDROCHLORINATION

PROCESS EMISSION SOURCE[a]	PLANT A		PLANT B		Comment on Plant Operation
	lb VCM/MM lb produced[b]	% VCM emissions	lb VCM/MM lb produced[b]	% VCM emissions	
Production Sources Emitting VCM					
EDC from Ethylene + Chlorine					
1. Reactor condenser vent,C	0(0)	--	0(0)	--	--
2. Crude reactor vent,C	0(0)[c]	--	0(0)[c]	--	--
3. Crude prod prim wash vessel vent,C	9.6-19.2(1-2)	0.4-0.5	9.6-19.2(1-2)	< 1	Water wash used.
4. Crude prod secdy wash vessel vent,C	0(0)	--	0(0)	--	Normally not vented.
5. Wash water, stripper, storage vent,C	9.6-58(1-6)	0.5-1.5	8.0-49(0.8-5)	0.5-1.5	--
6. Washed crude prod storage vent,C	0(0)[c]	--	0(0)[c]	--	--
7. Light-ends column condenser vent,C	240-1500(25-120)	13-38	240-1500(21-101)	13-38	--
8. Finishing column vent,C	0(0)	--	0(0)	--	--
9. Light-ends purification column vent,I	0-12(0-1.25)[d]	0-0.3	0-12(0-1.25)[d]	0-0.3	--
10. Refined EDC storage tank,C	0(0)[c]	--	0(0)[c]	--	--
11. Heavy-ends, tar-removal column vent,C	480-960(50-100)	24.8-26.4	480-960(42-84)	24.8-26.4	--
12. Heavy-ends storage tank,I	0(0)	--	0(0)	--	--
13. Tar storage tank,I	0(0)	--	0(0)	--	--
Total		40-65.9		40-65.9	
EDC from Ethylene + Hydrogen Chloride + Air					
14. Reactor vent,I	NA	--	NA	--	--
15. Reactor efflu refrig cond vent,C	154-230(16-24)	6-9	140-205(14-22)	6-9	--
Total		6-9		6-9	
VCM from Dehydrochlorination of EDC					
16. Light-ends distillation column vent,I	240-400(300-500)	10.3-13.2	2880-4800(252-420)	10.3-13.2	2 hr/day
17. Heavy-ends distillation column vent,I	14.1(2000)	< 1	13(1680)	< 1	3 min/mo
18. Heavy-ends, tar-removal column vent,C	Part of vent 11	--	Part of vent 11	--	--
19. Wastewater stripping column vent,C	Part of vent 5	--	Part of vent 5	--	--
Total		10.7-13.9		10.7-13.9	
Combined total, vents 1,7,9,11,15,16	3768-7502(391-748)	--	3768-7502(328-626)	--	--

Table 2-4. EMISSION RATES FOR VCM PROCESS 2: CHLORINATION-OXYCHLORINATION OF ETHYLENE (WITH AIR) AND DEHYDROCHLORINATION, Continued

PROCESS EMISSION SOURCE[a]	PLANT A		PLANT B		Comment on Plant Operation
	lb VCM/MM lb produced[b]	% VCM emissions	lb VCM/MM lb produced[b]	% VCM emissions	
Production Sources Emitting VCM, Cont'd.					
Scrubbing (vents 1,3,4,7,8,9,11,16,17)					
20. Scrubber tank vent, C	1540-2300(160-240)	--	1540-2300(134-202)	--	--
21. Tank-car Loading					
Purge, I	114(285)[e]	--	96(239)	--	2 hr/48 hr
Loading arm, I	16(20)	--	13(17)	--	2 hr/day
Tank-car slip gauge, I	48(120)	--	40(100)	--	1 hr/day
Refrigerated vent, I	192(300)	--	160(252)	--	16 hr/day
Total	370(440)	9.6-20.3	309(367)	9.6-20.3	
Fugitive Sources Emitting VCM					
Pumps, C	3.8(0.4)	--	3.8(0.4)	--	--
Pump maintenance, I	240 (25)	--	240 (25)	--	1 hr/mo
Valves, C	10 (1.04)	--	10 (1.04)	--	--
Relief valve, C	7.7(0.8)	--	7.7(0.8)	--	--
Cooling water, C	12 (1.25)	--	10 (1.05)	--	--
Samplers, C	20.8(2.16)	--	17.5(1.82)	--	--
Miscellaneous	10 (1.04)	--	8.5(0.88)	--	--
Total	304.3(6.69)[f]	7-17	297.5(5.99)[f]	7-17	

[a]C is continuous; I is intermittent. [b]Value in parentheses is lb VCM/hr released. [c]Vents 2,6, & 10 total 0-13 MSCFH. [d]Every 2 days, the 8-hr regeneration totals 0-10 lb. [e]To remove excess oxygen before reloading. [f]Total continuous; excludes intermittent pump maintenance.

Note: Plant C, with production capacity of 2.14 MM lb/day, has emission rate of 1368 lb VCM/MM lb produced (or 122 lb VCM/hr) for all sources except loading (830(1516); 4 hr/day, 100 day/yr) and the dock recovery vent (1087(2738); 290 days/yr.).

by gas chromatography, can be determined to 1 ppm ± 50 percent on "grab-bag" samples. The accuracy of the calculated data cannot be estimated with the information now available. Estimates for process upsets were not generally available. In one plant, pump maintenance was estimated as one pump per month at a VCM loss of 25 pounds. A report of one annual maintenance (during which all tanks, towers, and reactors were pumped out and residues vented to the atmosphere) estimated that 10,000 pounds of VCM had been lost into the environment in a 24-hour period; this procedure is now being revised, and a solvent absorption of residual VCM might be implemented.

Since VCM purification, storage, and transfer are carried out at high pressures to eliminate the need for relatively high-cost refrigeration systems, there exists a real potential for VCM losses from pressure leaks. The quantity of material lost from smaller or larger leaks in valves, pumps, and similar causes is variable from installation to installation and is largely determined by the quality of plant construction and maintenance. At best, only an average figure with a wide range can be assigned to this source of emission.

2.3.2 Controls and Costs

The control methods used depend on the level of emission and the possibility of recycling VCM to eliminate the emission source and to recover lost VCM. The state of the art controls described in the Table 2-5 should be applicable to any VCM production plants which have reported to this time, since the oxychlorination process and the controls used in at least some of these installations are basically similar. It is our belief that all producers can reduce the emissions in their plants significantly below

Table 2-5. CONTROLS AND COSTS FOR VCM PROCESS 2: CHLORINATION-OXYCHLORINATION OF ETHYLENE (WITH AIR) AND DEHYDROCHLORINATION

Emission Source Control	Percent Emission Reduction	Control Cost Estimate	Comment on Control Type
5. Wash Water, Stripper, Storage Vent: continuous stream; gas flow 300-2000 SCFH; 90°F			
Carbon bed adsorber	100		
Ozone oxidation	100		
7. Light-Ends Column Condenser Vent: continuous stream; 8000-500,000 SCFH			
Refrigerated condenser	50		
Carbon bed adsorber	100		
9. Light-Ends Purification Column Vent: intermittent stream; 21,000 lb hot N_2/8 hrs (10 lb VCM)			
Carbon bed adsorber	100	$50,000	Plus installation cost, purge, and recycle
Ozone oxidation	100		
15. Reactor Efflu Refrig Cond Vent: continuous stream; 13,000-15,000 SCFH; -13°F			
Additional oxychlorinator	90-93	$800,000	Includes all but adsorbent cost
Carbon bed, purge, recycle	100	$60,000	
16. Light-Ends Distillation Column Vent: intermittent stream			
Refrig cond and carb bed adsorber, or ozone oxid	100	$30,000-$150,000	
Incineration	95-98	$50,000	Cost depends on HCl recovery.
17. Heavy-Ends Distillation Column Vent: intermittent stream			
Incineration	93-95		
20. Scrubber Tank Vent: continuous stream; 500,000-800,000 SCFH; 40-100°F			
Refrigerated condenser	75-91	$30,000+	
Incineration	93-95		Cost depends on HCl recovery.
Refrigerated condenser and carb bed, purge, recycle	100	$30,000-$150,000	Depends on installation type. Depends on installation type.

Table 2-5. CONTROLS AND COSTS FOR VCM PROCESS 2: CHLORINATION-OXYCHLORINATION OF ETHYLENE (WITH AIR) AND DEHYDROCHLORINATION (continued)

Emission Source Control	Percent Emission Reduction	Control Cost Estimate	Comment on Control Type
21. Tank-Car Loading: intermittent stream; variable flow; 50-90°F			
Purge	50		
Vapor collection adapter	90		
Vapor collection, recycle			
Loading arm			
Incineration			Generates HCl.
Vapor collection adapter	90		
Slip gauge			
Thermal detector, recycle	95	$1,000	Cost per tank car loading line.
Magnetic gauge	100	$1,000	Cost per tank car.
Refrigerated vent			
Incineration, HCl recovery	97		Cost depends on HCl quantity.
22. Dock-VCM Revocery Vent: intermittent stream; 2700 lb/hr of loading			
Refrigerated condenser	98	$50,000	
25. Fugitive Sources: continuous and intermittent			
Pumps			
Pressurized mechanical seal	95		
Pump maintenance			
Valve and relief valve			
Diaphragm valve	95		
Double lock valve	50		
Rupt disc under relief valve	50		
Cooling water			
Sampler			
Vapor collectors	90	$1,000	
Miscellaneous	50	$40,000	Cost for 1/2 man-year labor.

50 ppm with state-of-the-art controls. However, thermal combustion of VCM produces hydrogen chloride, which is usually absorbed in water with a resulting production of hydrochloric acid; in operations without an outlet for the disposal of hydrochloric acid, this control method may not be applicable.

The need for development of longer term controls is not strongly indicated, pending the evaluation of data for state-of-the-art techniques. Scrubbing VCM process vents and washing equipment with EDC appears appropriate. Postchlorination units have reached the commercial market, and their value in reducing VCM emissions should be further investigated.

The costs of control methods depend on the magnitude of the emission to be controlled and the level to which the emission is to be controlled. These costs will vary from plant to plant, depending on the physical design of the plant. Estimates supplied by the reporting organizations are given. In only one instance have estimates been given by two manufacturers for control of the same emission source by the same control device; in this instance, the estimates were consistent within 7 percent.

2.4 CHLORINATION-OXYCHLORINATION OF ETHYLENE (WITH OXYGEN) AND DEHYDROCHLORINATION

One plant is currently using oxygen instead of air in the balanced hydrochlorination-oxychlorination process shown in Figures 2-5, 2-6, 2-7. The annual capacity of this VCM source is 300 million pounds.

2.4.1 Emission Points

The emission sources for this process are identical to those described in subsection 2.3.1. The volume of emissions are different because of the substitutions of 100 percent oxygen for the air mixture (80% N_2 + 20% O_2).

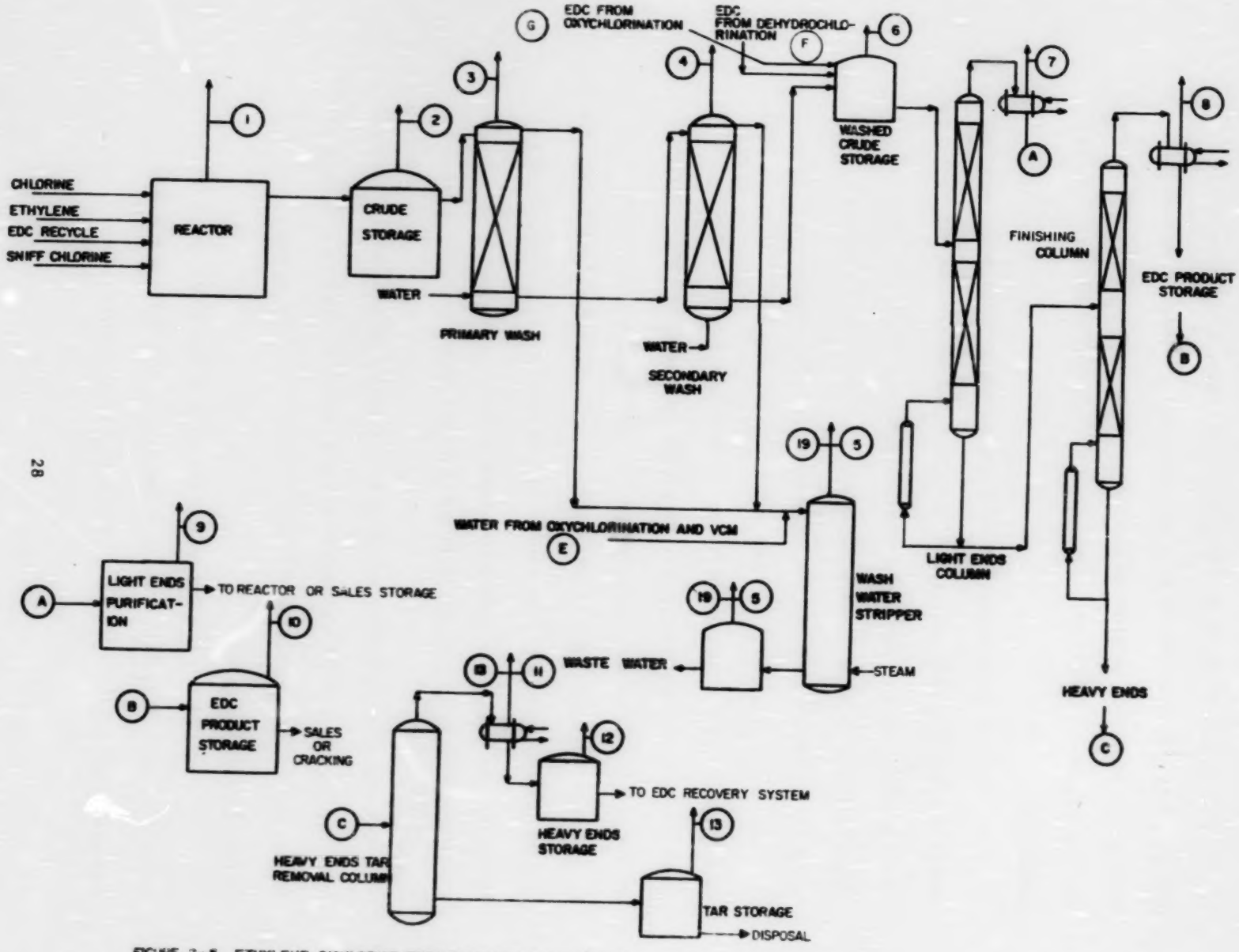

FIGURE 2-5 ETHYLENE DICHLORIDE FROM ETHYLENE AND CHLORINE

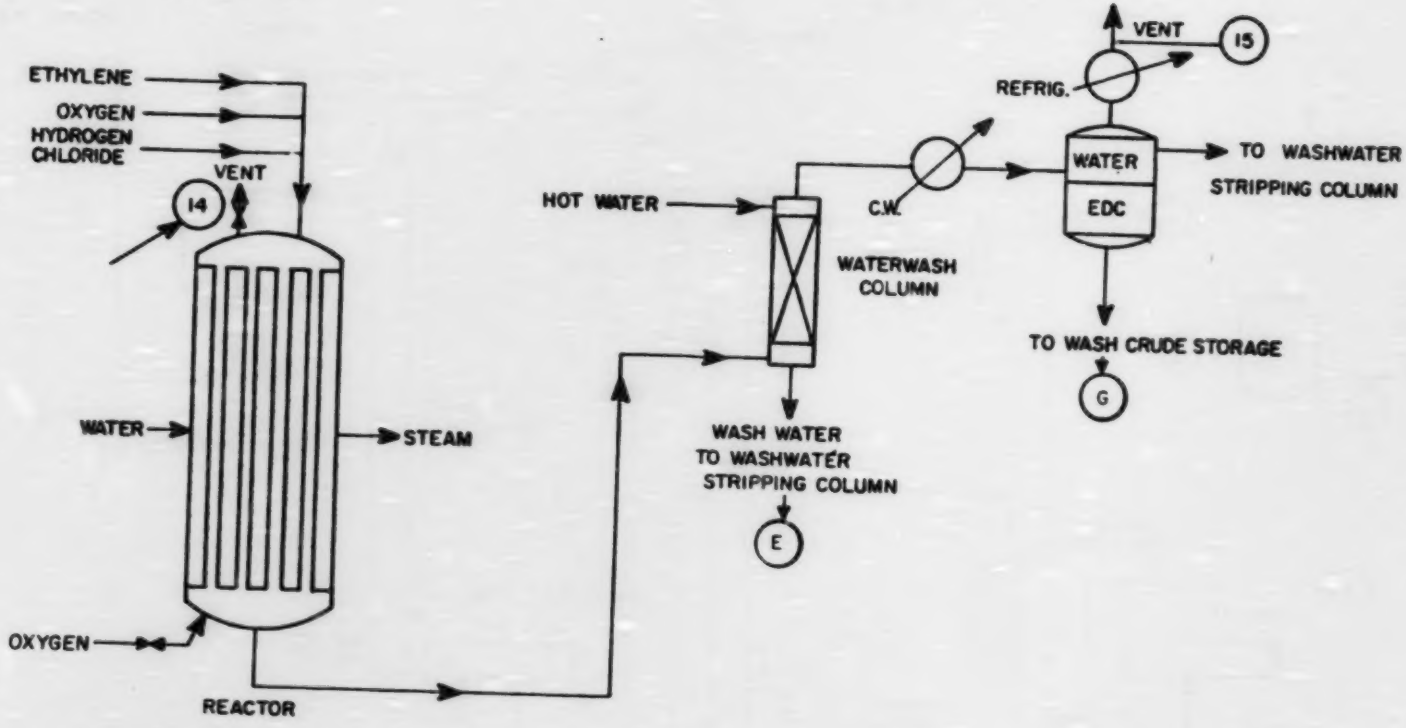

FIGURE 2-6 ETHYLENE DICHLORIDE FROM ETHYLENE + HCL + OXYGEN

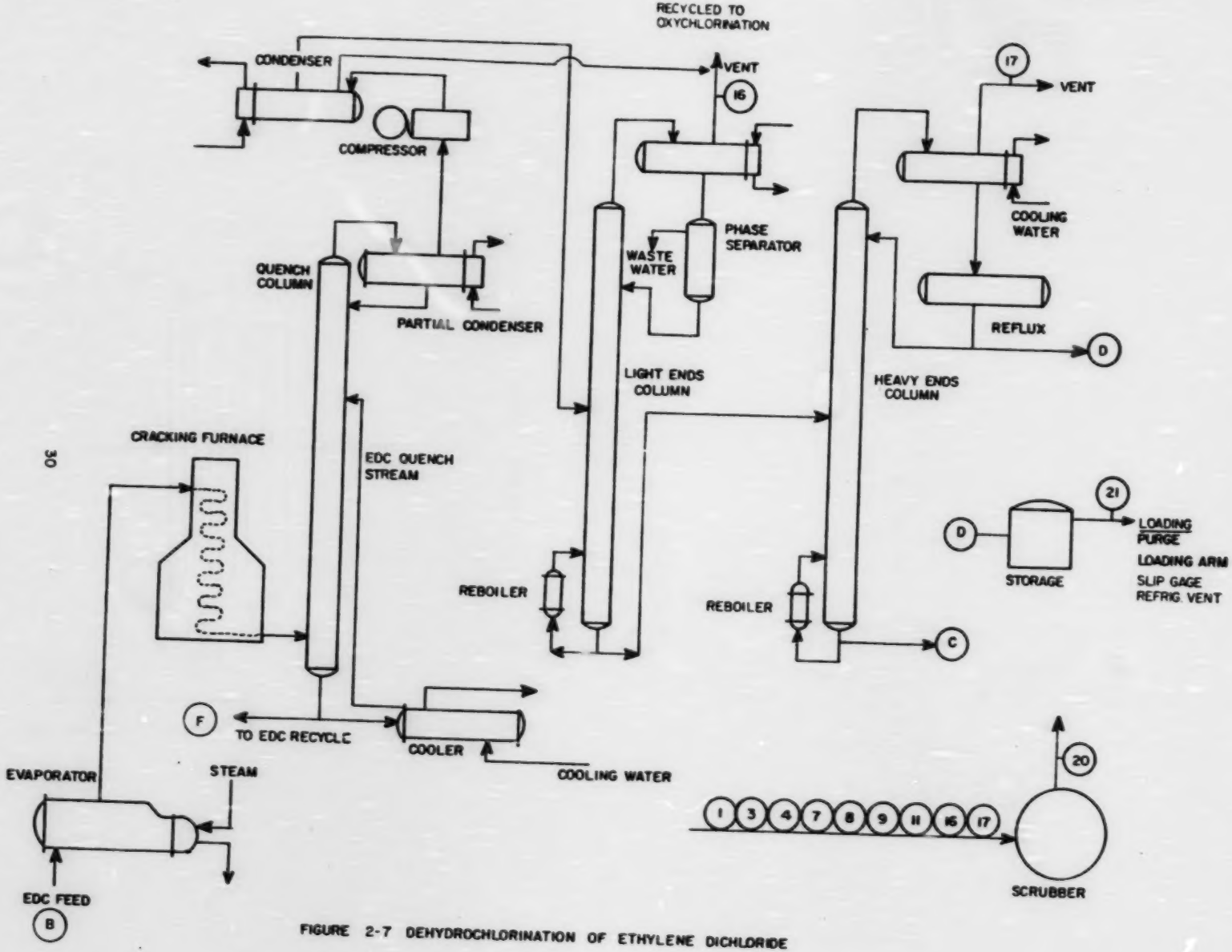

FIGURE 2-7 DEHYDROCHLORINATION OF ETHYLENE DICHLORIDE

The emission points designated in Table 2-6 are characterized by temperature, flow rate (continuous or intermittent), and percentage of VCM wherever data permit. The reliability of the data are provided at two levels: emissions quantities measured by standard methods to 1 ppm $\pm$ 0.5 ppm, and calculated and estimated values varying as much as 100 percent.

2.4.2 Controls and Costs

Based on the similarity of this process to that using air, the level of VCM emissions should be reduced with state of the art controls to 90-95 percent of the present levels, to significantly below 50 ppm and within the 5-50 ppm range. The state of the art controls (Table 2-7) are applicable to all plants using the balanced oxychlorination process, with either oxygen or air as the oxidant.

The use of oxygen instead of air is itself a long-term control, in the sense that it eliminates the effect of nitrogen on emissions. Nitrogen from air must be vented, under conditions that result in its being a carrier for vinyl chloride vapors.

The costs of reducing an emission to a level significantly below 50 ppm will vary from plant to plant, depending on the makeup of the process, cost of installation, and level of the emission. In general, considering cost of equipment and instrumentation, the cost of a 99 percent reduction of a principal emission source will range $50,000 to $100,000.

2.5 DIRECT CHLORINATION OF ETHYLENE, AND DEHYDROCHLORINATION

Direct chlorination and dehydrochlorination (Figures 2-8, 2-9) are used to produce VCM when the manufacturing plant has other uses for the hydrogen chloride byproduct. Three plants employ this approach to make approximately 700 million pounds of VCM a year.

2.5.1 Emission Points

Table 2-8 identifies the emission sources for both the production of

Table 2-6. EMISSION RATES FOR VCM PROCESS 3: HYDROCHLORINATION-OXYCHLORINATION OF ETHYLENE (WITH OXYGEN) AND DEHYDROCHLORINATION

PROCESS EMISSION SOURCE[a]	PLANT A		Comment on Plant Operation
	lb VCM/MM lb produced	% VCM emissions	
	Production Sources Emitting VCM		
EDC from Ethylene + Chlorine			
1. Reactor condenser vent, C			
2. Crude reactor vent, C			
3. Crude prod prim wash vessel vent, C			
4. Crude prod secdy wash vessel vent, C			
5. Wash water, stripper, storage vent, C			
6. Washed crude prod storage vent, C			
7. Light-ends column condenser vent, C			
8. Finishing column vent, C			
9. Light-ends purification column vent, I			
10. Refined EDC storage tank, C			
11. Heavy-ends, tar-removal column vent, C			
12. Heavy-ends storage tank, I			
13. Tar storage tank, I			
Total			
EDC from Ethylene + Hydrogen Chloride + Oxygen			
14. Reactor vent, I			
15. Reactor efflu refrig cond vent, C			
Total			
VCM from Dehydrochlorination of EDC			
16. Light-ends distillation column vent, I			
17. Heavy-ends distillation column vent, I			
18. Heavy-ends, tar-removal column vent, C			
19. Wastewater stripping column vent, C			
Total			
Combined total, vents 1,7,9,11,15,16			

Table 2-6. EMISSION RATES FOR VCM PROCESS 3: HYDROCHLORINATION-OXYCHLORINATION OF ETHYLENE (WITH OXYGEN) AND DEHYDROCHLORINATION (continued)

PROCESS EMISSION SOURCE[a]	PLANT A		Comment on Plant Operation
	lb VCM/MM lb produced	% VCM emissions	
	Production Sources Emitting VCM, cont'd.		
Scrubbing (vents 1,7,9,11,15,16)			
20. Scrubber tank vent, C			
21. Tank-car Loading			
Purge, I	114(285)[b]	--	2 hr/48 hr
Loading arm, I	16(20)	--	2 hr/day
Tank-car slip gauge, I	48(120)	--	1 hr/ day
Refrigerated vent, I	192(300)	--	16 hr/day
Total	370(440)	9.6-20.3	
	Fugitive Sources Emitting VCM		
Pumps, C	3.8(0.4)	--	
Pump maintenance, I	240(25)	--	
Valves, C	10(1.04)	--	
Relief valve, C	7.7(0.8)	--	
Cooling water, C	12(1.25)	--	
Samplers, C	20.8(2.16)	--	
Miscellaneous	10(1.04)	--	
Total	304.3(6.69)	7-17	

[a] C is continuous, I is intermittent.

[b] Data from Table 2-4 are shown here; they are believed to be transferable to this plant.

Table 2-7. CONTROLS AND COSTS FOR VCM PROCESS 3: CHLORINATION-OXYCHLORINATION OF ETHYLENE (WITH OXYGEN) AND DEHYDROCHLORINATION

Emission Source Control	Percent Emission Reduction	Control Cost Estimate	Comment on Control Type
5. Wash Water, Stripper, Storage Vent: continuous stream			
Carbon bed adsorber Ozone oxidation			
7. Light-Ends Column Condenser Vent: continuous stream			
Refrigerated condenser Carbon bed adsorber			
9. Light-Ends Purification Column Vent: intermittent stream			
Carbon bed adsorber Ozone oxidation			
15. Reactor Efflu Refrig Cond Vent: continuous stream			
Additional oxychlorinator Carbon bed, purge, recycle			
16. Light-Ends Distillation Column Vent: intermittent stream			
Refrig cond and carb bed adsorber, or ozone oxid Incineration			
17. Heavy-Ends Distillation Column Vent: intermittent stream			
Incineration			
20. Scrubber Tank Vent: continuous stream			
Refrigerated condenser Incineration Refrigerated condenser and carb bed, purge, recycle			

Table 2-7. CONTROLS AND COSTS FOR VCM PROCESS 3: CHLORINATION-OXYCHLORINATION OF ETHYLENE (WITH OXYGEN AND DEHYDROCHLORINATION (continued)

Emission Source Control	Percent Emission Reduction	Control Cost Estimate	Comment on Control Type
21. Tank-Car Loading: intermittent stream; variable flow			
Purge			
Vapor collection adapter	90[a]		
Vapor collection, recycle			
Loading arm			
Incineration	90		Generates HCl
Vapor collection adapter			
Slip gauge			
Thermal detector, recycle	95	$1000	Cost per tank car loading line
Magnetic gauge	100	$1000	Cost per tank car
Refrigerated vent			
Incineration, HCl recovery	97		Cost depends on HCl quantity
22. Dock-VCM Recovery Vent: intermittent stream			
Refrigerated condenser	98	$50,000	
25. Fugitive Sources: continuous and intermittent			
Pumps			
Pressurized mechanical seal	95		
Pump maintenance			
Valve and relief valve			
Diaphragm valve	95		
Double lock valve	50		
Rupt disc under safety valve	50		
Cooling water			
Sampler			
Vapor collector	90	$1000	
Miscellaneous	50	$40,000	Cost for 1/2 - man year labor

[a]Data from Process 1

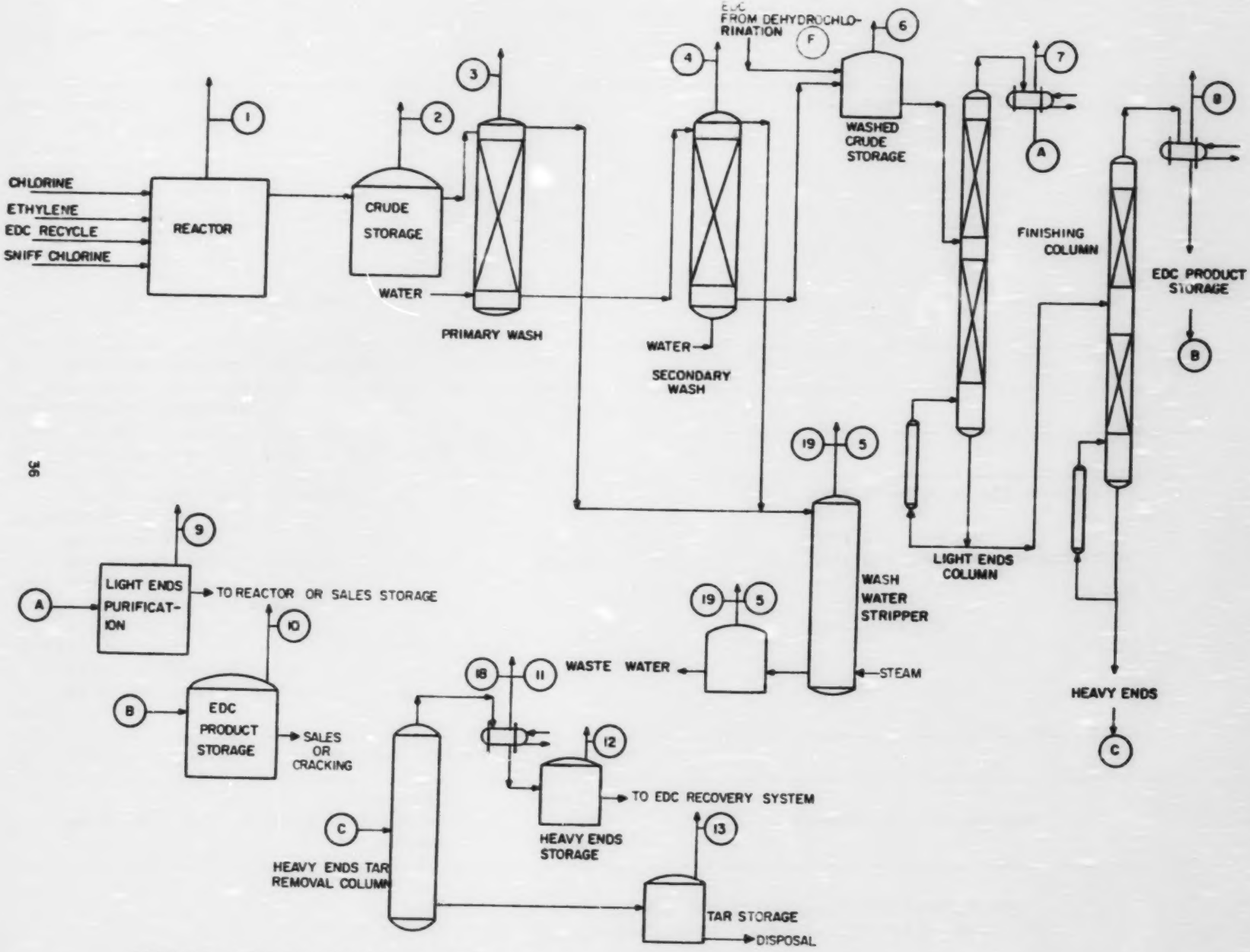

FIGURE 2-8. ETHYLENE DICHLORIDE FROM ETHYLENE AND CHLORINE

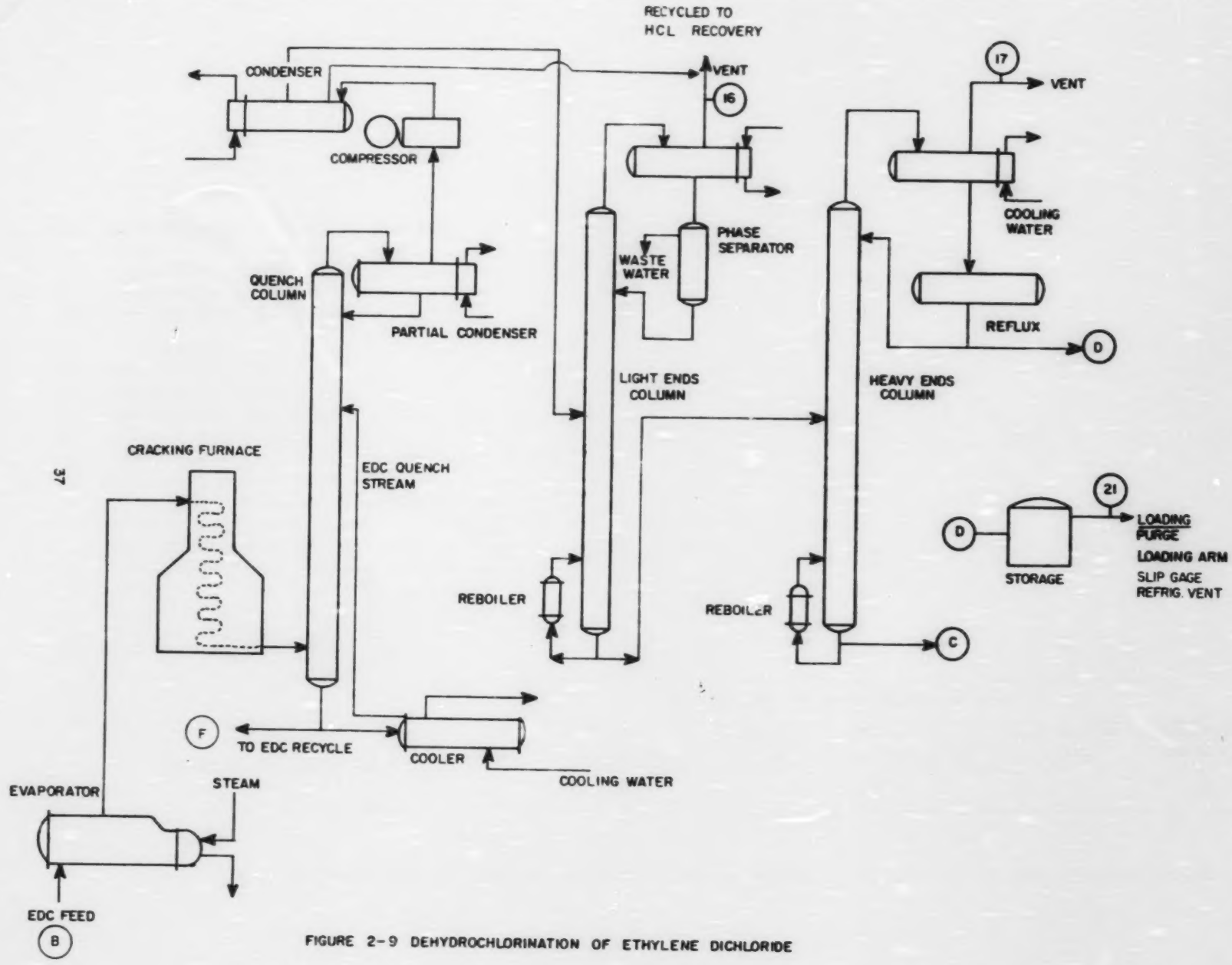

FIGURE 2-9 DEHYDROCHLORINATION OF ETHYLENE DICHLORIDE

Table 2-8. EMISSION RATES FOR VCM PROCESS 4: DIRECT CHLORINATION OF ETHYLENE, AND DEHYDROCHLORINATION

PROCESS EMISSION SOURCE[a]	PLANT A		PLANT B		
	lb VCM/MM lb produced[b]	% VCM emissions	lb VCM/MM lb produced[b]	% VCM emissions	Comment on Plant Operation
Production Sources Emitting VCM					
EDC from Ethylene+ Chlorine					
1. Reactor condenser vent, C					
2. Crude reactor vent, C					
3. Crude prod prim wash vessel vent, C					
4. Crude prod secdy wash vessel vent, C					
5. Wash water, stripper, storage vent, C					
6. Washed crude prod storage vent, C					
7. Light-ends column condenser vent, C					
8. Finishing column vent, C					
9. Ligh-ends purification column vent, I					
10. Refined EDC storage tank, C					
11. Heavy-ends, tar-removal column vent, C					
12. Heavy-ends storage tank, I					
13. Tar storage tank, I					
Total					
VCM from Dehydrochlorination of EDC					
16. Light-ends distillation column vent, I					
17. Heavy-ends distillation column vent, I	Part of vent 11		Part of vent 11		
18. Heavy-ends, tar-removal column vent, C	Part of vent 3		Part of vent 3		
19. Wastewater stripping column vent, C					
Total					

Table 2-8. EMISSION RATES FOR VCM PROCESS 4: DIRECT CHLORINATION OF ETHYLENE, AND DEHYDROCHLORINATION (continued)

PROCESS EMISSION SOURCE[a]	PLANT A		PLANT B		
	lb VCM/MM lb produced[b]	% VCM emissions	lb VCM/MM lb produced[b]	% VCM emissions	Comment on Plant Operation
Production Sources Emitting VCM, cont'd					
21. Tank-car loading					
Purge, I	114(285)				2 hr/48 hr
Loading arm, I	16(20)				2 hr/day
Tank-car slip gauge, I	48(120				1 hr/day
Refrigerated vent, I	192(300)				16 hr/day
Total	370(440)				4 hr/day, 100 day/yr
Fugitive Sources Emitting VCM					
Pumps, C	(52)				
Pump maintenance, I	(16)				
Relief valve, C	(3)				
Cooling water, C					
Sampler, C	(6)				
Miscellaneous					
Total					

[a] C is continuous, I is intermittent; sources 14, 15, and 20 do not exist for this process.

[b] Value in parentheses is lb VCM/hr released.

EDC by direct chlorination and the dehydrochlorination of EDC to VCM. The emission points are characterized by flow rate, temperature, total emissions, and percentage of VCM to the extent data permit. Where data are available, two levels of reliability can be indicated: "measured" data are considered reliable and "estimated" data (based on material balances) are considered to have an error of at least 100 percent. This information is to be given in Table 2-8. (Note: no data are available at this time).

Those producers making EDC by direct chlorination only are reported to have < 0.1 of the emissions associated with the use of oxychlorination. They do however need to recycle EDC from their dehydrochlorination process to the direct chlorination system for recovery. This causes VCM emissions from the crude EDC-refining system.

2.5.2 Controls and Costs

Neither the reactor vent nor the crude reactor would be expected to contain VCM, since the crude product is subjected either to wash purification or to anhydrous purification; however, no data are available on the control of these sources. It is at this point that EDC recycled from the dehydrochlorination process would likely be introduced; again, data on emission levels and controls are not available at this time.

While state of the art controls appear to be adaptable to most emission sources, certain controls (especially adsorption) must be adapted with careful consideration of their relation to the rest of the plant. Thus one plant proposes to use adsorption instead of the present refrigerated condenser on the vinyl chloride light-ends column. They find it appropriate to desorb with ethane and to compress the stripped gases for recycle.

Controls and cost information are tabulated in Table 2-9, both to the extent available.

Table 2-9. CONTROLS AND COSTS FOR VCM PROCESS 4: DIRECT CHLORINATION OF ETHYLENE, AND DEHYDROCHLORINATION

Emission Source Control	Percent Emission Reduction	Control Cost Estimate[a]	Comment on Control Type
5. Wash Water, Stripper, Storage Vent: continuous stream			
Carbon bed adsorber			
Ozone oxidation			
9. Light-Ends Purification Column Vent: intermittent stream			
Carbon bed adsorber			
Ozone oxidation			
16. Light-Ends Distillation Column Vent: intermittent stream			
Refrigerated condenser and carbon bed adsorber			
Incineration			
17. Heavy-Ends Distillation Column Vent: intermittent stream			
Vented to gas holder, recycle			
21. Tank-Car Loading: intermittent stream			
Purge			
Vapor collection adapter	90[a]		
Vapor collection, recycle			
Loading arm			
Incineration			
Vapor collection adapter	90		Generates HCl

[a]Data are from Process 1.

Table 2-9. CONTROLS AND COSTS FOR VCM PROCESS 4: DIRECT CHLORINATION OF ETHYLENE, AND DEHYDROCHLORINATION (continued)

Emission Source Control	Percent Emission Reduction	Control Cost Estimate	Comment on Control Type
21. Tank-Car Loading: intermittent stream			
Slip gauge			
Thermal detector, recycle	95	$1000	Cost per tank car loading line
Magnetic gauge	100	$1000	Cost per tank car
Refrigerated vent			
Incineration, HCL recovery	97		Cost depends on HCl quantity
22. Dock-VCM Recovery Vent: intermittent			
Refrigerated condenser	98	$50,000	
25. Fugitive Sources: continuous and intermittent			
Pumps			
Pressurized mechanical seal	95		
Pump maintenance			
Valve and relief valve			
Diaphragm valve	95		
Double lock valve	50		
Rupt disc under safety valve	50		
Cooling water			
Sampler			
Vapor collector	90	$1000	
Miscellaneous	50	$40,000	Cost for 1/2 man-year labor

3. POLYVINYLCHLORIDE

3.1 OVERVIEW OF PROCESSES

A typical PVC plant includes the following operations:

1. Receiving and storage of VCM and catalysts.
2. Polymerization of VCM: measuring and charging, and reaction.
3. Stripping and recovery: reactor blowdown and recovery, and slurry handling and storage.
4. Centrifugation or filtration.
5. Drying.
6. Pneumatic conveying and storage.
7. Packaging and shipping.
8. Blending.
9. Waste treatment.

Compounding, which may be done in a PVC resin plant or in separate facilities, is not included in this study.

Total PVC output for 1972-73 is attributed to four process types: suspension polymerization, 78 percent; emulsion polymerization, 12 percent; bulk polymerization, 6 percent; and solution polymerization, 4 percent. All polymerizations in the United States are batch operations, which probably contribute strongly to the severity of the VCM emissions problem.

3.2 SUSPENSION POLYMERIZATION

The 34 suspension plants now in operation are producing 75-85 percent of the PVC produced.

3.2.1 Emission Points

Suspension polymerization (Figure 3-1) uses a water media, a suspension agent such as polyvinyl alcohol, and an oil-soluble catalyst. A typical recipe is 100 parts VCM, 200 of water, 0.1-0.2 of catalyst, and 0.005-0.0 of suspension agent. The VCM-water ratio can be varied over a wide range; the limiting factor is sufficient fluidity of the final PVC-water slurry, for adequate dissipation of the heat evolved during polymerization. Oil-soluble

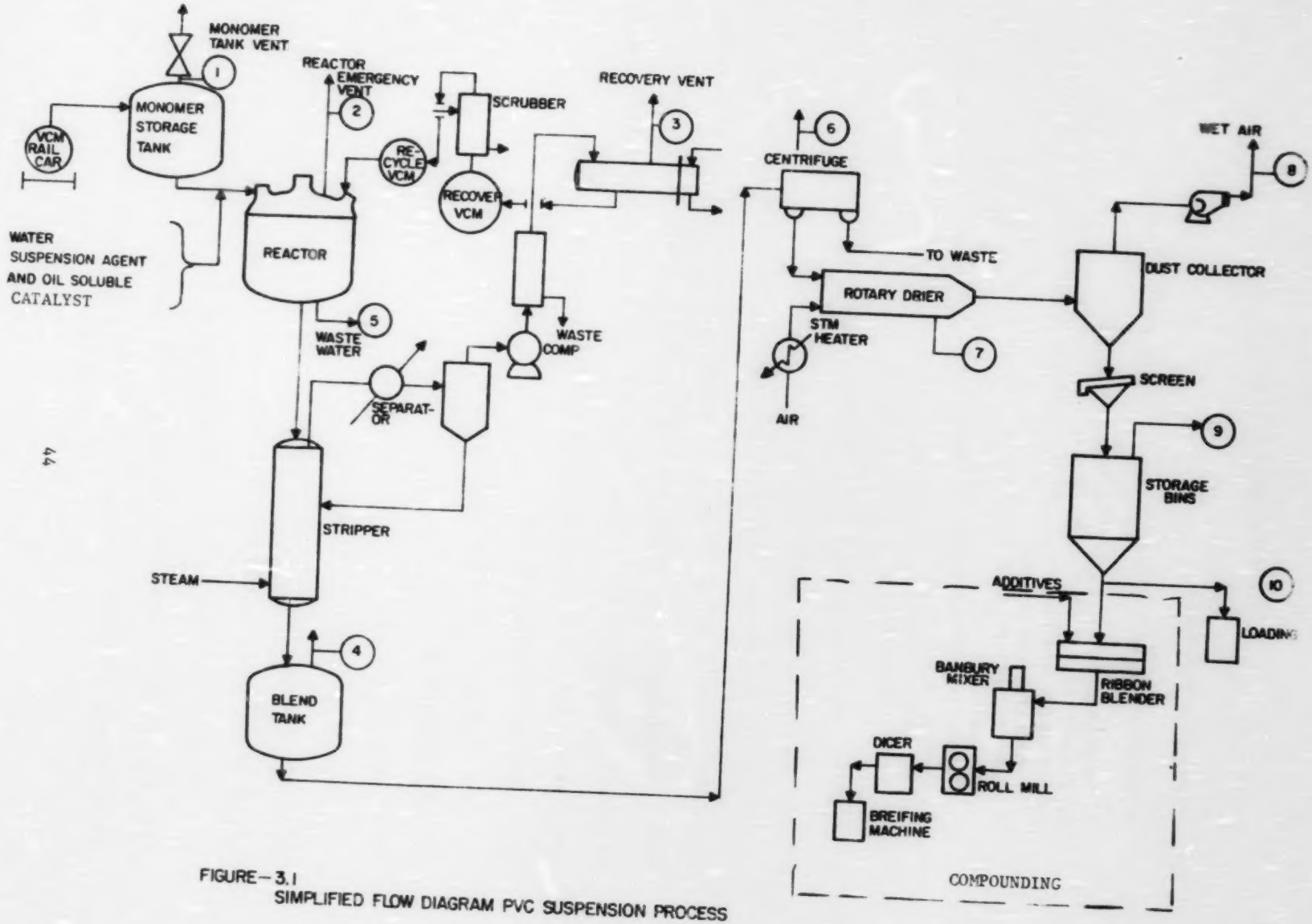

FIGURE – 3.1
SIMPLIFIED FLOW DIAGRAM PVC SUSPENSION PROCESS

catalysts such as dibenzoyl peroxide, acetyl benzoyl peroxide, or dibutyl peroxide are preferred to the water soluble persulfate catalyst. Persulfate is slower, and it produces particles too fine to be handled in conventional filtering and drying equipment.

Commercial suspension resins show little or no retention on a 100-mesh (U.S. standard) screen and from 30 to 80 percent retention on a 200-mesh screen. Such a particle size is achieved by rapid agitation in glass-lined autoclaves at 35 to 45°C. Vigorous agitation suspends VCM as fine droplets in water, controls size, and gives a granular polymer for better filtering and drying.

During polymerization, alkaline buffers such as sodium carbonate, bicarbonate, and phosphate have been used to maintain the pH at 5-8 to prevent formation of hydrochloric acid. Use of an inert substance such as nitrogen increases reaction rate, reduces the amount of hydrochloric acid evolved, and thereby increases the stability of the polymer.

There is little published information on molecular weight distribution and chain branching of vinylchloride polymers. However, chloride polymers in general have narrow molecular distributions, especially compared to those of polystyrene.

The major advantage of suspension polymerization is the excellent heat transfer rate attainable in conventional equipment. The major disadvantage is that water must be separated from the polymer, usually by centrifugation and drying.

Table 3-1 indicates 34 suspension plants producing 3.5 billion pounds a year. In Table 3-2 the VCM emissions rates are given for the sources shown in Figure 3-1; the table is restricted to those plants for which data have been supplied.

Table 3-1. VCM EMISSIONS DATA FROM PVC PLANTS

Company Name and Location		City Population (1970 census)	PVC Capacity (MM lb/yr)	VCM Emissions[a] (MM lb/yr)	Type of Process[b]
Air Products and Chemicals, Inc Plastics Division	Calvert City, Ky Pensacola, Fla	31,627[c] 59,507	120 50	4.8 2.0	S S
American Chemical Corp[d]	Long Beach, Calif	358,633[e]	125	5.0	S
Borden, Incorporated Borden Chemical Division	Illiopolis, Ill Leominster, Mass	1,122 32,939	285	11.4	S&E
Continental Oil Company Conoco Plastics Division	Aberdeen, Miss Oklahoma City, Okla	6,157[f] 366,481[f]	220 80	8.8 3.2	S&E S&E
Diamond Shamrock Corp Diamond Shamrock Chem Co (Subsid Plas Div)	Delaware City, Del Deer Park, Tex	2,024 12,773[g]	250	10.0	S&E
Ethyl Corp (Industrial Chemical Div)	Baton Rouge, La	165,963[h]	180	7.2	S&E
The Firestone Tire and Rubber Company Chemical Plastics Division	Perryville, Md Pottstown, Pa	2,091 25,355	130 140	5.2 5.6	S&E&SL (10)
The General Tire & Rubber Co (Chem/Plas Div)	Ashtabula, Ohio	24,313	100	4.0	
The B.F. Goodrich Company	Long Beach, Calif	358,633[e]	125	5.0	S&E&
B.F. Goodrich Chemical Company	Henry, Ill	2,610[i]	125	5.0	B(40)
B.F. Goodrich Chemical Company	Louisville, Ky	361,472	275	11.0	SL(20)
B.F. Goodrich Chemical Company	Avon Lake, Ohio	12,261	125	5.0	
B.F. Goodrich Chemical Company	Pedricktown, NJ		130	5.2	
The Goodyear Tire & Rubber Company Chemical Division	Plaquemine, La Niagara Falls, NY	7,739[j] 85,615	100 100	4.0 4.0	S&E& B(40)
Great American Chemical Corp	Fitchburg, Mass	43,343	40	1.6	S
Keysor-Century Corporation	Saugus, Calif	[e]	35	1.4	S
Monsanto Company (Poly and Petro-Chem Co)	Springfield, Mass	163,905	150	6.0	S&E
National Starch and Chemical Corp	Meredosia, Ill	1,178	10	0.4	E
Occidental Petroleum Corp Hooker Chemical Corp (Subsid Ruco Div)	Burlington, NJ Hicksville, NY	11,991[k] 48,075	180 10	7.2 0.4	S&B (160)

Table 3-1. VCM EMISSIONS DATA FROM PVC PLANTS, Continued

Company Name and Location		City Population (1970 census)	PVC Capacity (MM lb/yr)	VCM Emissions[a] (MM lb/yr)	Type of Process[b]
Olin Corp (Thompson Plastics Company Div)	Assonet, Mass		150	6.0	S
Pantasoto Company	Passaic, NJ	55,124	120	4.8	E
Pantasoto Company	Point Pleasant, WVA	6,122			
Robintech, Inc	Painesville, Ohio	16,536	250	10.0	S
Stauffer Chemical Company (Plastics Div)	Delaware City, Del	2,024	160	6.4	S
Tenneco Chemicals, Inc	Burlington, NJ	11,991[k]	165	6.6	S&E
Tenneco Plastics Division	Flemington, NJ	3,917	60	2.4	S&E
Tenneco Plastics Division	Pasadena, Tex	89,277[g]	300	12.0	S&E
Union Carbide Corp	Texas City, Tex	38,908	200	8.0	S&E
Chemicals and Plastics Division	So Charleston, WVA	16,333	120	4.8	(120)
Uniroyal Chemicals, Inc.	Painesville, Ohio	16,536	140	5.6	S&E
Subtotal (plants in operation)			4,750	190.0	
Certainteed Corporation	Lake Charles, La	77,978	200	8.0	U
Georgia Pacific	Plaquemine, La	7,739	200	8.0	U
Shintech	Oyster Creek, Tex	11,997	250	10.0	U
Subtotal (plants under construction)			650	26.0	
Total			5,400	216.0	

[a] Extrapolations based on est'd 4.0% VCM emission from PVC production (industry total 224 lb/yr) and recovery.

[b] B bulk, E emulsion, SL solution, S suspension, U unknown; value in parentheses, est'd process production(MM lb

[c] Population of Paducah, Ky. [d] Joint venture: Atlantic Richfield & Stauffer Chem. [e] Los Angeles County - 7,032,0

[f] Oklahoma County - 526,805. [g] Harris County - 1,741,912. [h] Baton Rouge Parrish (county) - 302,031.

[i] Henry County - 53,217. [j] Plaquemine Parrish (county) - 25,225. [k] Burlington County - 323,132.

Table 3-2. EMISSION RATES FOR PVC SUSPENSION PROCESS

PROCESS EMISSION SOURCE[a]	PLANT A		PLANT B	
	lb VCM/MM lb produced[b]	% VCM emissions	lb VCM/MM lb produced[b]	% VCM emissions
1. VCM tank vent, C	Part of vent 15		Part of vent 15	
2. Reactor emergency vent, I	Part of vent 15		Part of vent 15	
3. VCM recovery still vent, C	Part of vent 15		Part of vent 15	
4. Blend or surge tank vent, C	4280(48.2)	11.0	3447(34.5)	11.5
5. Wastewater, VCM recovery, C				
6. Centrifuge vent, C	Part of vent 9		Part of vent 9	
7. Dryer vent, C	Part of vent 9		Part of vent 9	
8. Air conveyor vent, C	Part of vent 9		Part of vent 9	
9. Storage bin vent, C	13,498(152.0)	35.0	7872(78.8)	23
10. VCM loading, storage vents, I	Part of vent 15		Part of vent 15	
11. VCM charging, I	Part of vent 15		Part of vent 15	
12. Polymerizer cleaning, I	3019(34.0)	7.8	3447(34.5)	10-12
13. Packing/hopper car, I	1243(14.0)	3.2	300(3.0)	1
14. System cleaning, I	Part of vent 15		Part of vent 15	
15. Fugitive losses, C&I	17,467(196.7)	40-46	18,691(187.1)	50-58
16. Abnormal losses, I				
Total	39,507(444.9) or 3.5% VCM in PVC		33,757(337.9) or 3.0% VCM in PVC	

[a] C is continuous, I is intermittent.

[b] Value in parentheses is lb VCM/hr.

Note: Plant C with a capacity of 175 MM lb/yr emitted 7079 lb VCM/MM lb(155 lb VCM/hr) from vent 1 and 2283 lb VCM/MM lb(50 lb VCM/hr) from vent 4; emissions totaled 24.2% for vent 1 and 7.8% for vent 4.

3.2.2 Controls and Costs

Emissions may be reduced by process modifications, but these possibilities are excluded from the summary table--not because modifications are less important but because they can have impacts on product quality and thus need more detailed evaluation to justify inclusion. Of all the process modifications, vacuum stripping after polymerization is one of the most important. At least two companies are practicing this method in emulsion PVC polymerization, just as in suspension polymerization. This should be considered a state of the art control. The cost for retrofitting vacuum stripping is guestimated at $250,000-$500,000 per unit.

Emissions may be combined; the combined airstreams may be treated at less cost than individual ones. Control methods may be combined and/or used in sequence; for example, ozonation is expensive, but may be efficient as a final step to destroy VCM. All of these should be considered in the developmental stage and in need of evaluation.

Table 3-3 gives an assessment (qualitative) of state of the art control techniques. Economics and control levels are included to the extent they are available.

3.3 EMULSION POLYMERIZATION

The 11 emulsion plants operating at present contribute 12 percent of the PVC being produced.

3.3.1 Emission Points

The emulsion process (Figure 3-2) is similar to the suspension process (Figure 3-1). In emulsion, the particle size is smaller. Emulsifiers and additives maintain a nonsettling emulsion during polymerization. At least four components are needed--water, VCM, water soluble initiators, and an

Table 3-3. CONTROLS AND COSTS FOR PVC SUSPENSION PROCESS

Emission Source Control	Percent Emission Reduction[a]	Control Cost Estimate[b]	Comment on Control Type
3. VCM Recycle Column Vent: continuous; 0.017-0.019 lb VCM/lb prod[c,d]; 50-80°F; 80-150 psig; variable flow			
Vacuum stripping	50-80		
Carbon bed	50-99		
Incineration	50-99		
Absorption	50-90		
Refrigeration	40-60		
4. Blend or Surge Tank Vent: continuous stream; 0.0043-0.0035 lb VCM/lb prod[c,d]; 80-130°F, 0-10 psig; variable fl			
Vacuum stripping	50-80[e]		As a process change, may affect product quality.
Recycle to compressor	40-60		
Carbon bed	50-99		
Ozone oxidation	50-99		
Incineration	50-99		
Absorption	50-80		
Refrigeration	40-60		
5. Wastewater, VCM Recovery: continuous; NA[f]; variable flow			
Stream stripping	50-90		
Carbon bed	50-99		
Ozone oxidation	50-99		
6. Centrifuge Vent: continuous stream; NA[f]; 80-130°F; 0-5 inches of water, variable flow			
Vacuum stripping	50-80[e]		May affect product quality; surface filters may cause VCM emiss
Recycle to compressor	40-60		
Carbon bed	50-99		
Ozone oxidation	50-99		
Incineration	50-99		
Absorption	50-80		
Refrigeration	40-60		

Table 3-3. CONTROLS AND COSTS FOR PVC SUSPENSION PROCESS (continued)

Emission Source Control	Percent Emission Reduction[a]	Control Cost Estimate[b]	Comment on Control Type
7. Dryer Vent: continuous stream; NA[f]; 100-150°F, 0-2 inches of water; flow--10,000-30,000 SCFM/dryer			
Vacuum stripping	50-80		--
Higher air recycle	40-80		--
Carbon bed	50-99		Applied after water removal
Ozone oxidation	50-99		--
Absorption	50-90		--
8. Air Conveyor Vent: continuous; NA[f]; 70-120°F, 0-2 inches of water; variable flow			
Vacuum stripping	50-80		--
Recycle	50-99		--
9. Storage Bin Vent: continuous; NA; 70-120°F; 0-2 inches of water; variable flow			
Vacuum stripping	50-80[e]		As a process change, may affect product quality.
Recycle	50-95		--
Incineration	50-95		--
10. VCM Loading, Storage Vents: intermittent; NA[d]; 60-80°F, 20-50 psig; variable flow			
Recycle	50-80		--
Absorption	50-90		--
11. VCM Charging: intermittent; NA[d]; 60-80°F, 25-50 psig; variable flow			
Recycle, padded transfer	$\geq$50-90		--
Absorption	$\geq$50-90		--

Table 3-3. CONTROLS AND COSTS FOR PVC SUSPENSION PROCESS (continued)

Emission Source Control	Percent Emission Reduction[a]	Control Cost Estimate[b]	Comment on Control Type
12. Polymerizer Cleaning: intermittent; NA[d]; variable flow			
		--	High pressure cleaning systems coming into use.
13. Packing/Hopper Car: intermittent; NA; ambient temperature; 0 psig; variable flow			
Vacuum stripping	50-80[e]		As a process change, may affect quality.
Wood and recycle	50-60	--	
14. System Cleaning: intermittent; NA; variable flow			
Evacuate vessels	50-60		Evacuated before cleaning.
15. Fugitive Losses[g]: variable; highly variable; ≥ 60% of total emission losses; low data reliability			
16. Abnormal Losses[h]: emergency or abnormal, NA; highly variable (0 - 150 lb/hr)			

[a]All reductions are with cost trade-offs.

[b]NA is not available.

[c]Calculated VCM-production values (good data NA) include fugitive losses.

[d]Substantial upset losses possible.

[e]Range for VCM reduction after the reactor.

[f]Some upset losses possible.

[g]Valves packing glands; pump, agitator, and compressor seals; safety and blowout valves; screwed and welded piping leaks; flange and instrument connections.

[h]Relief valve losses from VCM storage tanks, polymerizers, blowdown tanks, VCM-recovery compressor discharges crude-VCM storage tanks, and VCM distillation system; operational error; tank or vessel rupture.

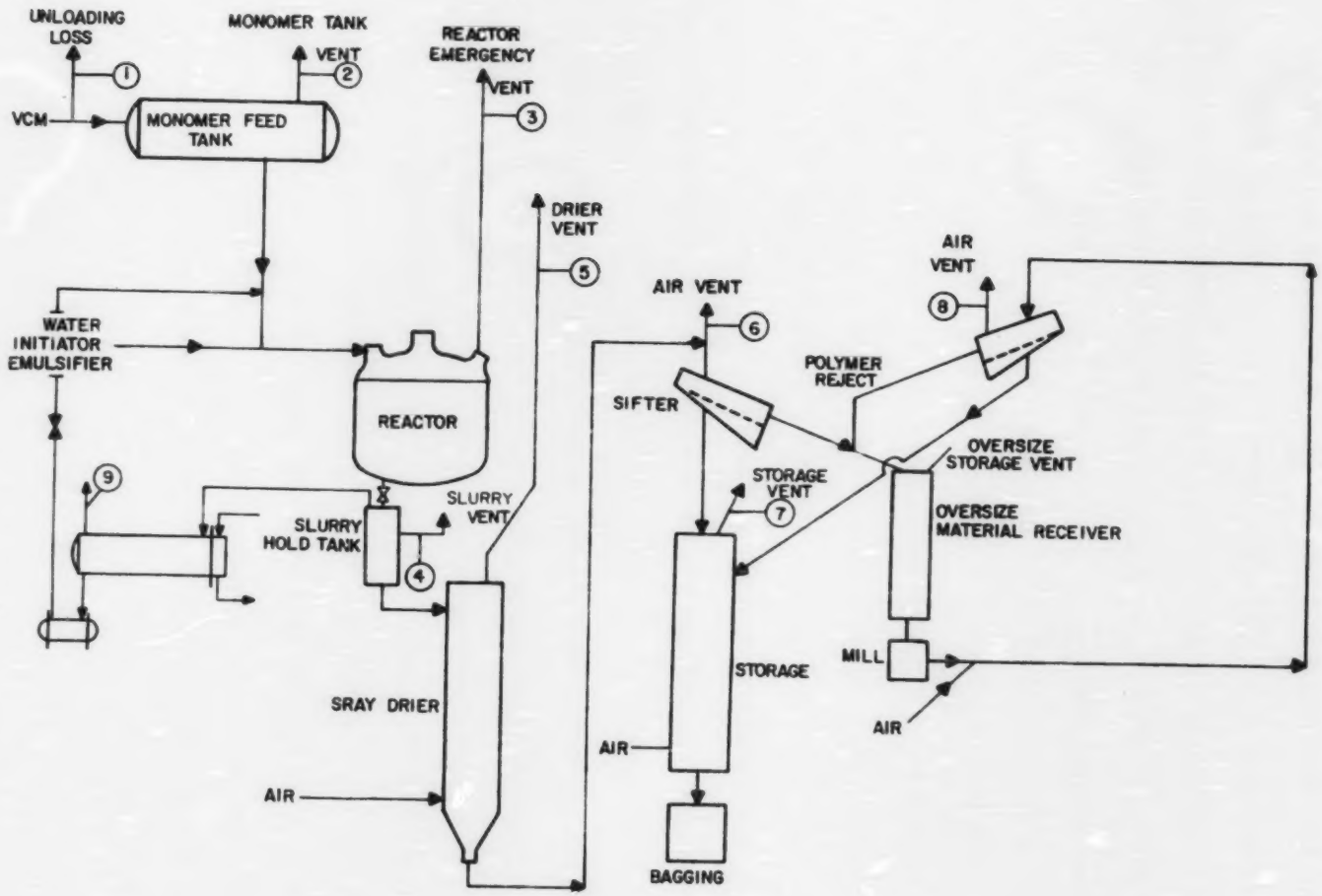

FIGURE 3.2 SIMPLIFIED FLOW DIAGRAM BATCH EMULSION POLYMERIZATION OF VINYL CHLORIDE

emulsifying agent. Water is the continuous phase; VCM is the discontinuous phase. Low concentrations of emulsifiers (either anionic or cationic) behave essentially as electrolytes because they are uniformly distributed between the water-VCM phases. When the concentration is increased, the surface tension between the phases decreases and the conductivity of the mixture increases. Above a critical concentration, the surface tension and conductivity change less rapidly and the emulsifier begins to agglomerate into groups of 20-30 molecules called micelles. In the water phase, the initiator forms a free radical which migrates to the micelles, combines with the VCM molecules, and begins the polymer chain. That is, a polymer particle starts to form, the emulsifier collects at the surface, and the VCM molecules diffuse (from the dispersed VCM droplets) through the water phase and through the emulsifier to the growing polymer chain.

As polymerization of VCM progresses and as the other polymer particles grow, more emulsifier is needed at the particle surfaces. In some cases when 1-2 percent conversion is reached, the emulsifier micelles disappear and all of the emulsifier is concentrated at the particle surfaces; at higher conversions, perhaps 60 percent, all of the VCM is in the PVC phase. The number of PVC particles formed (i.e., their size) seems to be controlled in the early stages of polymerization. Termination steps involving coupling or disproportionation are rare because the number of PVC chains for each particle is small. Hence, PVC produced by the emulsion process tends to have high molecular weights. In principle, the process can be continuous; however, only the batch operation is practiced in the United States.

Table 3-1 lists the 11 emulsion plants operating at present. Total production figures are not yet available. In Table 3-4, the VMC emissions are given as pounds of VCM per million pounds of PVC produced and as total pounds of VCM released per hour. The VCM emissions sources and rates are restricted to those plants for which data have been received. The data show that VCM emissions are about 4 percent of the VCM feed; this emissions level is similar to that observed for suspension polymerization. However, data from additional plants are needed to draw a firm conclusion regarding the range and reliability of the emission levels.

3.3.2 Controls and Costs

Control techniques available for each emission source will be categorized and rated in summary Table 3-5 when data becomes available.

Emissions may be reduced by process modifications, but these possibilities are excluded from the summary table--not because modifications are less important but because they can have impacts on product quality and thus need more detailed evaluation to justify inclusion. Of all the process modifications, vacuum stripping after polymerization is one of the most important. At least two companies are practicing this method in emulsion PVC polymerization, just as in suspension polymerization. This should be considered a state of the art control. The cost for retrofitting vacuum stripping is guestimated at $250,000-$500,000 per unit.

Emissions may be combined; the combined airstreams may be treated at less cost than individual ones. Control methods may be combined and/or used in sequence; for example, ozonation is expensive, but may be efficient as a final step to destroy VCM. All of these should be considered in the developmental stage and in need of evaluation.

Table 3-4. EMISSION RATES FOR PVC EMULSION PROCESS

PROCESS EMISSION SOURCE[a]	PLANT A		PLANT B	
	lb VCM/MM lb produced[b]	% VCM emissions	lb VCM/MM lb produced[b]	% VCM emissions
1. Unloading losses, I	Part of vent 9		Part of vent 9	
2. VCM feed tank vent, I	Part of vent 9		Part of vent 9	
3. Reactor emergency vent, I				
4. Slurry hold tank vent, C	219(1.0)	0.6	3026(11.4)	7.2
5. Dryer vent, C	10,293(490)	25.6	35,570(134.0)	84.0
6. Air conveyor vent, C				
7. Storage vent, C				
8. Resin-screening vent, C				
9. VCM recovery vent, C	26,958(1231)	76.0	796(3.0)	1.9
10. Polymerizer cleaning, I	2738(12.5)	6.8		
11. Packing/hopper car, I				
12. System cleaning, I				
13. Fugitive losses, C&I			2920(11.0)	6.9
14. Abnormal losses, I				
Total	40,208(183.6)		42,312(159.4)	

[a] C is continuous, I is intermittent.

[b] Value in parentheses is lb VCM/hr.

Table 3-5. CONTROLS AND COSTS FOR PVC EMULSION PROCESS

Emission Source Control	Percent Emission Reduction	Control Cost Estimate	Comment on Control Type
1. Unloading Losses: intermittent stream			
2. VCM Feed Tank Vent: intermittent stream			
3. Reactor Emergency Vent: intermittent stream			
4. Slurry Hold Tank Vent: continuous stream			
5. Dryer Vent: continuous stream			
6. Air Conveyor Vent: continuous stream			
7. Storage Vent: continuous stream			

Table 3-5. CONTROLS AND COSTS FOR PVC EMULSION PROCESS (continued)

Emission Source Control	Percent Emission Reduction	Control Cost Estimate	Comment on Control Type
8. Resin-Screening Vent: continuous stream			
9. VCM Recovery Vent: continuous stream			
10. Polymerizer Cleaning: intermittent stream			
11. Packing/Hopper Car: intermittent stream			
12. System Cleaning: intermittent stream			
13. Fugitive Losses: continuous and intermittent			
14. Abnormal Losses: intermittent			

3.4 BULK POLYMERIZATION

The 3 bulk polymerization plants are producing 300 million pounds of PVC a year.

3.4.1 Emission Points

In bulk polymerization (Figure 3-3), only VCM and small amounts of additives are charged to the reactors; inert diluents such as water or solvents are not used. The Pechiney-St. Gobain bulk polymerization process consists of two stages. In the prepolymerizer, the additives are slurried in monomer, which is then about 10 percent converted to insoluble polymer. In the autoclave, VCM is polyerized in a "paste" phase to obtain 90 percent conversion.

The advantages claimed are (1) no impurities in the final PVC and (2) low capital and operating costs because separation of an inert diluent is not required.

Table 3-6 shows that three plants are operating bulk polymerization of VCM. Data from only one company is available. In Table 3-7, the VCM emissions are given in pounds of VCM per million pounds of PVC produced and as total pounds of VCM released per hour.

3.4.2 Controls and Costs

The economically attractive bulk polymerization may offer more

Table 3-6. PRODUCTION CAPACITIES OF BULK PLANTS

Company	Location	Amount
The B. F. Goodrich Company	NA	40 MM lb/yr
The Goodyear Tire and Rubber Company	NA	80 MM lb/yr
Occidental Petroleum Corporation	Burlington, N.J.	180 MM lb/yr

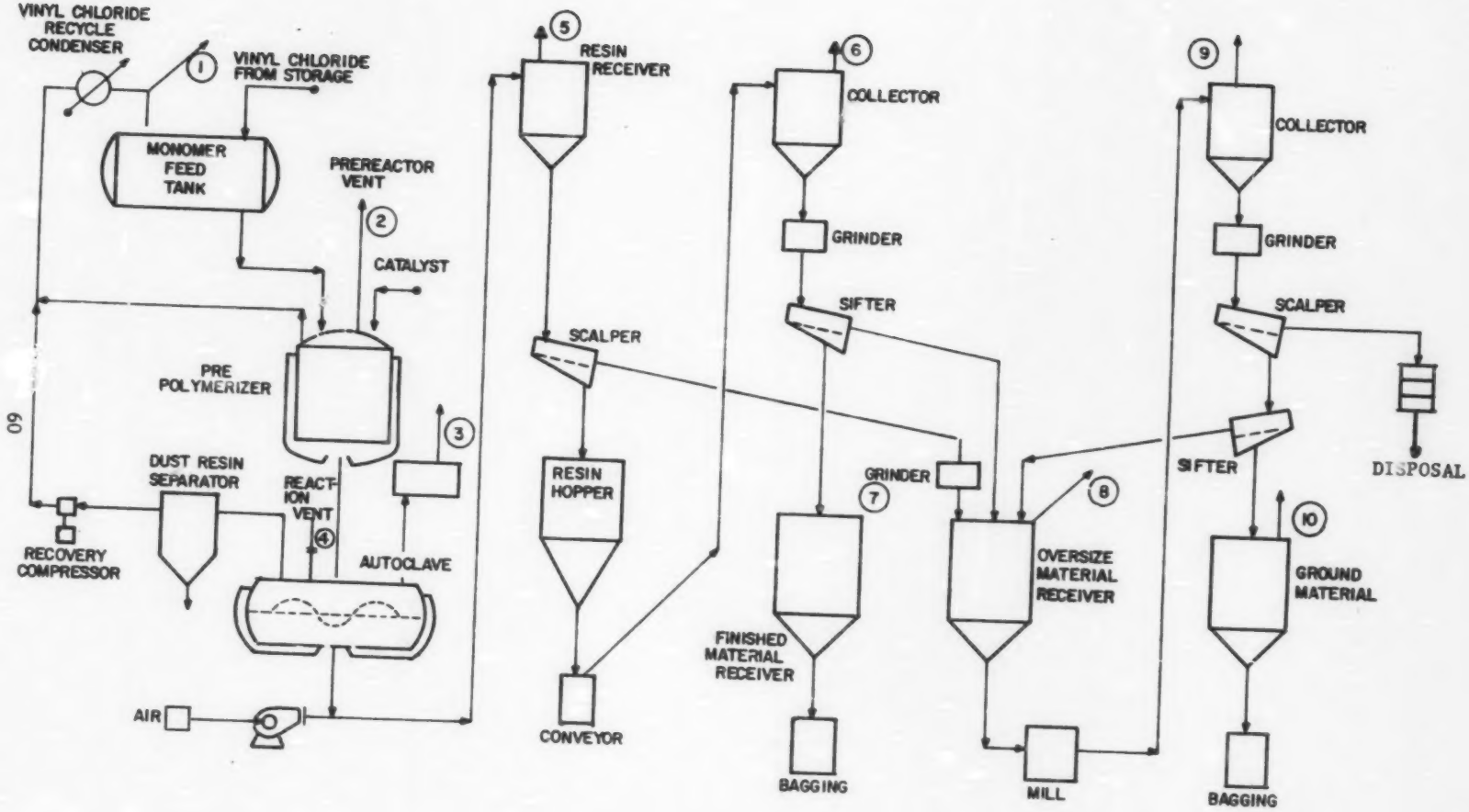

FIGURE 3.3 SIMPLIFIED FLOW DIAGRAM BULK POLYMERIZATION OF VINYL CHLORIDE

Table 3-7. EMISSION RATES FOR PVC BULK PROCESS

PROCESS EMISSION SOURCE[a]	PLANT A			Comment
	lb VCM/MM lb produced	lb VCM/hr emitted	% VCM emissions	
1. VCM feed tank vent, I	7900	29.1	33	
2. Prereactor vent, I	Part of vent 3	Part of vent 3		
3. Reactor, I	2800	10.3	12	
4. Reactor emergency vent, I	0	0	0	
5. Resin receiver vent, C	2000	7.4		
6. Resin collector vent, C	Part of vent 5	Part of vent 5		
7. Finished product storage vent, C	Part of vent 5	Part of vent 5	20	
8. Oversized PVC storage vent, C	Part of vent 5	Part of vent 5		
9. Second collector vent, C	Part of vent 5	Part of vent 5		
10. Ground material vent, C	Part of vent 5	Part of vent 5		
11. Fugitive losses, C&I	800	29.4	35	
Total	13,500	76.2[b,c]		

[a] C is continuous, I is intermittent.

[b] PVC emitted at 2800 lb VCM/MM lb produced (10.3 lb VCM/hr emitted).

[c] Or 3.1% VCM in PVC.

resistance to a reduction of emissions than suspension polymerization. Dry steam may enhance the vacuum stripping action and reduce strongly the VCM emission. For all other emissions, controls similar to those described in sections 3.2 and 3.3 can be used (Table 3-8).

3.5 SOLUTION POLYMERIZATION

Three solution polymerization plants (Table 3-9) are producing 150 million pounds of PVC a year.

3.5.1 Emission Points

Solution polymerization (Figure 3-4) is often conducted in systems where PVC is slightly soluble in the solvent and VCM is soluble. The products tend to have low molecular weights because the solvents act to some extent as chain transfer agents; therefore, straight comparisons with the other polymerization methods are not possible.

Absence of water simplifies the recovery of the final product and is the major advantage for this process. If a volatile solvent like N-butane is used, unreacted VCM and solvent are easy to remove.

No data are available on solution polymerization. Table 3-10 provides for future data on sources shown in Figure 3-4; it does not give any actual data. Total losses are expected to be approximately 2-3 percent

Table 3-9. PRODUCTION CAPACITIES OF SOLUTION PLANTS

Company	Location	Amount
The Firestone Tire and Rubber Company	NA	10 MM lb/yr
The B.F. Goodrich Company	NA	20 MM lb/yr
Union Carbide Corporation	NA	120 MM lb/yr

Table 3-8. CONTROLS AND COSTS FOR PVC BULK PROCESS

Emission Source Control	Percent Emission Reduction	Control Cost Estimate	Comment on Control Type
1. VCM Feed Tank Vent: intermittent stream			
2. Prereactor Vent: intermittent stream			
3. Reactor: intermittent stream			
4. Reactor Emergency Vent: intermittent stream			
5. Resin Receiver Vent: continuous stream			
6. Resin Collector Vent: continuous stream			

Table 3-8. CONTROLS AND COSTS FOR PVC BULK PROCESS (continued)

Emission Source Control	Percent Emission Reduction	Control Cost Estimate	Comment on Control Type
7. Finished Product Storage Vent: continuous stream			
8. Oversized PVC Storage Vent: continuous stream			
9. Second Collector Vent: continuous stream			
10. Grounded Material Vent: continuous stream			
11. Fugitive Losses: continuous and intermittent streams			

FIGURE 3.4 SIMPLIFIED FLOW DIAGRAM
-SOLUTION POLYMERIZATION
PROCESS FOR PVC

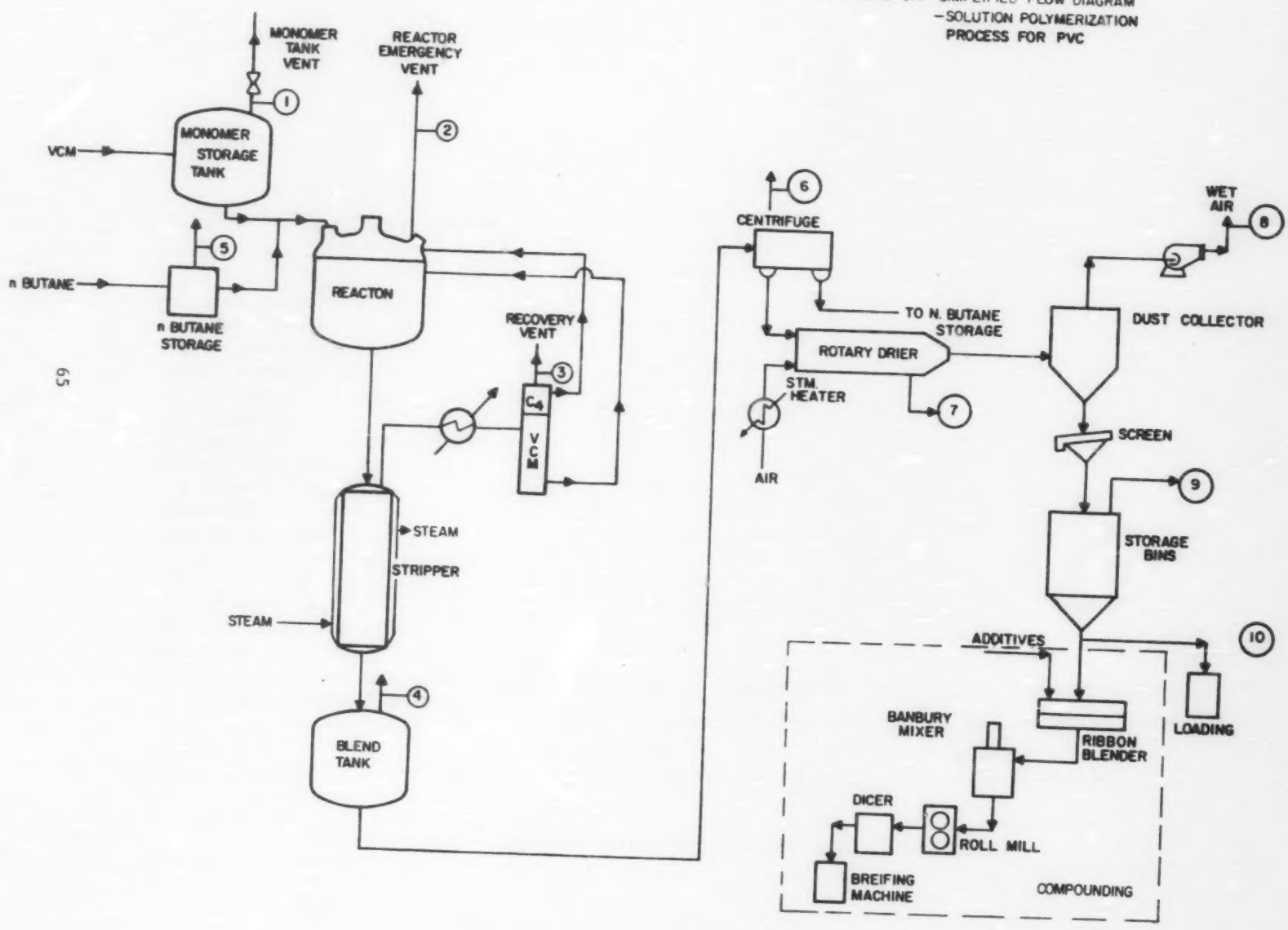

Table 3-10. EMISSION RATES FOR THE PVC SOLUTION PROCESS

PROCESS EMISSION SOURCE[a]	PLANT A		PLANT B	
	lb VCM/MM lb produced	% VCM emissions	lb VCM/MM lb produced	% VCM emissions
1. VCM tank vent, C				
2. Reactor emergency vent, I				
3. VCM recovery still vent, C				
4. Blend or surge tank vent, C				
5. Solvent storage tank vent, C				
6. Centrifuge vent, C				
7. Dryer vent, C				
8. Air conveyor vent, C				
9. Storage bin vent, C				
10. VCM loading, storage tank vents, I				
11. VCM charging, I				
12. Polymerizer cleaning, I				
13. Packing/hopper car, I				
14. System cleaning, I				
15. Fugitive losses, C&I				
16. Abnormal losses, I				
Total				

[a]C is continuous, I is intermittent.

VCM and 1 percent PVC fines on PVC produced. Reduction should be by control steps similar to those indicated for the suspension process.

3.5.2 Controls and Costs

Presently, the solution process probably leads to a PVC recovery of 96-97 percent of VCM intake. Most likely, the actual VCM losses total 2-3 percent. These losses are not specified as to different vent streams. Table 3-11 shows controls that are believed to be appropriate.

Table 3-11. CONTROLS AND COSTS FOR PVC SOLUTION PROCESS

Emission Source Control	Percent Emission Reduction	Control Cost Estimate	Comment on Control Type
1. VCM Tank Vent: continuous stream; inerts + VCM; -13°F, 60-150 psig			
2. Reactor Emergency Vent: intermittent stream			
Carbon bed adsorption	50-90		
Incineration	50-99		With or without water wash.
Ozone oxidation			High cost anticipated.
Absorption	50-90		
3. VCM Recovery Still Vent: continuous stream; variable flow			
4. Blend or Surge Tank Vent: continuous stream			
5. Solvent Storage Tank Vent: continuous stream			
6. Centrifuge Vent: continuous stream			
Vacuum stripping	50-80		May affect product quality.
Water sprayer			Effectiveness to be determined.
Total recycle with bleed stream			Long-range control type.

Table 3-11. CONTROLS AND COSTS FOR PVC SOLUTION PROCESS (continued)

Emission Source Control	Percent Emission Reduction	Control Cost Estimate	Comment on Control Type
7. Dryer Vent: continuous stream			
Vacuum stripping	50-80		
Carbon bed adsorption	50-99		
Ozone oxidation	50-99		
Absorption	50-80		
Water sprayer			Effectiveness to be determined.
Total recycle with bleed stream			Long-range control type.
8. Air Conveyor Vent: continuous stream			
Vacuum stripping	50-80		
Carbon bed adsorption	50-99		
Incineration	50-99		
Water sprayer			Effectiveness to be determined.
Total recycle with bleed stream			Long-range control type.
9. Storage Bin Vent: continuous stream			
Vacuum stripping	50-80		
Carbon bed adsorption	50-99		
Incineration	50-99		
Water sprayer			Effectiveness to be determined.
Total recycle with bleed stream			Long-range control type.
10. VCM Loading, Storage Tank Vent: intermittent stream			
Recycle	50-80		
Absorption	50-80		

Table 3-11. CONTROLS AND COSTS FOR PVC SOLUTION PROCESS (continued)

Emission Source Control	Percent Emission Reduction	Control Cost Estimate	Comment on Control Type
11. VCM Charging: intermittent stream			
12. Polymerizer Cleaning: intermittent stream			
13. Packing/Hopper Car: intermittent stream			
14. System Cleaning: intermittent stream			
15. Fugitive Losses: continuous and intermittent			
Pumps			
Pump maintenance			
Valve and relief valve			
diaphragm valves	50		
packed seals	50		
rupt disc under relief valve			
Miscellaneous			
preventive maintenance	50		
16. Abnormal Losses: intermittent			

4. SUMMARY OF ASSESSMENT AND FUTURE NEEDS

4.1 RESULTS OF PRODUCTION-EMISSION ASSESSMENT

The VCM emissions total about 3000 pounds per million pounds of VCM produced. To this amount should be added an on-the-average smaller, intermittent VCM loss from the loading area; a 90 percent reduction of this amount can be obtained relatively straightforwardly by refrigeration and/or absorption of VCM in the vents that are heavy in appropriate solvents (EDC for instance) and by combustion of the organics and HCl-removal in other vent streams. A 99 percent reduction is about the limit of present-day technology; to achieve this, the loading area would definitely have to be policed for vent losses.

In PVC production, the pounds of VCM losses per pound of PVC are at least an order of magnitude higher than those from VCM production. Most producers report PVC production as 3-4 percent lower than VCM intake, and some producers report 1-1.5 percent of PVC production lost as fines to the atmosphere. Thus, the actual VCM losses (2-3%) result from the batch operation of the polymerization and in the filtration and the drying of the polymer. Direct reduction to 50 percent of the present level seems possible, but a 90 percent reduction without process changes in some existing PVC plants is likely to be beyond present control techniques and acceptable costs. However, intensive stripping at the end of the suspension reaction may achieve the 90 percent reduction at acceptable costs.

Controls appraised for VCM production sources include recycling of vent streams, condensation with refrigeration, compression, adsorption with carbon, incineration, oxidation with ozone, absorption (scrubbing), and venting to flares. Monomer loading (and unloading) involves special

controls: vapor collection adapters with recycling, thermal level detectors with recycling, and magnetic gauges. The PVC production sources can benefit from the same controls plus vacuum stripping of crude product, steam stripping, and carrier airstream recycling. Fugitive sources require use of better valves, packings, etc.

Cost data received from VCM and PVC production show wide variation without direct comparison. Since the limited cost data (none for pollution control) were usually based on modifications of the existing system, the estimates received were simply recorded in the tables dealing with state of the art controls in sections 2 and 3.

4.2 RESULTS OF SOURCE-CONTROL ASSESSMENT

A qualitative assessment of the potential applications of selected controls was based on information presented to date (June 1974) by U.S. industrial firms. The results of this assessment are summarized for each of eight VCM and PVC production processes. All percentage reductions of emissions are estimates.

4.2.1 VCM from Hydrochlorination of Acetylene (Process 1)

The vent-gas reactor vent, which is the main emissions source, accounts for 60 percent of total emissions. Condensation at 40°F and 35 psi is now being used. Addition of refrigeration would decrease emissions 50 percent; addition of an HCl scrubber should achieve 85 percent reduction; these, combined with carbon adsorption, should reduce emissions 99 percent. Recycling, incineration, ozone oxidation, and venting to flares do not appear to be applicable.

Fugitive emissions equal about 25 percent of total emissions. Use of diaphragm on double lock valves, replacement of packed pump seals with

pressurized mechanical seals, use of vapor collectors on samplers, and preventive maintenance should reduce these emissions 50-95 percent.

Tank-car loading accounts for about 13 percent of emissions. Incineration, with HCl recovery should reduce loading arm emissions 90 percent and condenser vent losses 99 percent. Thermal level detectors with recycling would reduce slip gages 95 percent and magnetic gages 100 percent. Vapor collection adapters with recycling would reduce purge losses 50-90 percent.

4.2.2 VCM from Chlorination-Oxychlorination of Ethylene (Using Air) and Dehydrochlorination (Process 2)

Major emission sources are the EDC light-ends condenser column vent (13-38%), the heavy-ends, tar-removal column vent (25-26%), the VCM light-ends distillation column vent (10-13%), and the tank-car loading (10-20%).

EDC light-ends column emissions could be reduced 50 percent by refrigerated condensers and 100 percent by either carbon adsorption or recycle to a postchlorination unit. Heavy-ends column emissions are believed to be controllable by incineration (90% reduction) and by adsorption (100% reduction). For VCM light ends, either adsorption or ozone oxidation would achieve 100 percent reduction. Tank-car loading controls for VCM process 1 would apply here.

4.2.3 VCM from Chlorination-Oxychlorination of Ethylene (Using Oxygen) and Dehydrochlorination

Major emission sources and controls are believed to be essentially the same as those for process 2. Use of oxygen would reduce the amounts of vent streams from the oxychlorination process and thus would reduce emissions somewhat.

4.2.4 VCM from Direct Chlorination of Ethylene and Dehydrochlorination

The controls and reductions appear to be the same as for process 2

for VCM emissions. Incineration (light-ends column) with HCl-recovery by scrubbing is about 90 percent efficient for avoiding HCl emissions.

4.2.5 VCM from Suspension Polymerization

Fugitive emissions account for 12-46 percent of total emissions. Vacuum stripping of the crude product would reduce these emissions 50-80 percent; carbon adsorption, 50-99 percent; condensation with refrigeration, 40-60 percent; incineration, 50-99 percent; and absorption, 50-90 percent.

Collectively, the dryer vents, the air conveyor vent, the storage bin vent, and the centrifuge vent provide 35 percent of the total emissions. Vacuum stripping could achieve 50-80 percent reduction, and either carbon adsorption, ozone oxidation, incineration, steam stripping, or recycling to compressors would reduce emissions 40-99 percent. Air recycle should reduce these emissions 40-80 percent.

Blend surge tanks account for 11 percent of total emissions. Carbon adsorption, ozone oxidation, and incineration should give 50-99 percent reductions. Vacuum stripping and absorption are expected to give 50-80 percent; recycles to compressors, 40-60 percent.

4.2.6 VCM from Emulsion Polymerization

The dryer vent, the air conveyor vent, the storage vent, and the VCM recovery vent appear to account collectively for up to 85 percent of total emissions. Carbon adsorption, ozone oxidation, and steam stripping could reduce these emissions 50-99 percent. Absorption might achieve 90 percent. The recycle of airstreams could be 40-80 percent efficient.

Fugitive losses contribute 3 percent of the emissions and the resin receiver vents contribute another 7 percent. For either source, vacuum stripping, would effect 50-80 percent reduction; carbon adsorption, 50-99

percent. Condensation with refrigeration would reduce either source 40-60 percent; absorption, 50-80 percent. Preventive maintenance, would reduce fugitive losses 25-50 percent. The surge tank vents could be recycled (40-60% reduction) or oxidized with ozone (50-99% reduction).

4.2.7 VCM from Bulk Polymerization

The VCM reactor vent (12 percent), fugitive emissions (35 percent), and the combined resin receiver, collector, and storage (20 percent) are the major emission sources. For the reactor vent, adsorption could achieve 50-90 percent reduction. Intensive maintenance is believed to be capable of giving 50-75 percent reduction of the diverse, ill-defined fugitive emissions (which need further study). The product-collection systems vents could be water washed and then adsorbed (50-90% reduction), oxidized with ozone (90% reduction), or incinerated (50-90% reduction).

4.2.8 VCM from Solution Polymerization

While no data are available at present, solution polymerization is expected to have the emission characteristics of the suspension polymerization process and to respond similarly to the same controls.

4.3 RESEARCH AND DEVELOPMENT NEEDS

The information needs identified during this study include performance data, basic data and cost data. Performance data are needed to quantify PVC buildup during adsorption with activated carbon and to identify, if possible, uses which would improve the effectiveness of this control. If the proposed larger PVC reactors (120,000 gallons instead of the present 5-10,000) are put into use, emergency blowing may lead to high peak values for VCM emissions. Not considered in this study is the effect of VCM emissions (sometimes 1000 ppm) remaining in the PVC; release of most of

this may cause emission problems during further processing. Also needed are basic data on the effectiveness of sprayers in removing solids from vent gases of the PVC processes and on the use of EDC as an absorbent for vent gases of the VCM processes. The impact of process modifications on the quality of PVC products must be determined more precisely before the adsorption by such control techniques can be recommended.

The costs and benefits of the use of oxygen instead of air for the oxychlorination of ethylene should be quantified. This technique should be compared with the use of postchlorination units.

Cost data are needed that distinguish between capital equipment investments made primarily for recovery of unreacted VCM and those investments made solely for reduction of emissions. Possibly, the total costs for reactor vent streams can be reduced by the value of the recovered VCM. Investments already made should be distinguishable from new costs for additional control equipment.